Normal & Reversed Spin Mobility in a Diradical By Electron-Vibration Coupling

Yi Shen

University of Electronic Science and Technology of China (UESTC)

Guodong Xue

University of Electronic Science and Technology of China (UESTC)

Yasi Dai

Università di Bologna

Sergio Moles Quintero

University of Málaga

Hanjiao Chen

Sichuan University

Dongsheng Wang

University of Electronic Science and Technology of China

Fang Miao

University of Electronic Science and Technology of China

Fabrizia Negri

Univ. Bologna <https://orcid.org/0000-0002-0359-0128>

Yonghao Zheng

University of Electronic Science and Technology of China <https://orcid.org/0000-0003-1931-3536>

Juan Casado Cordon (✉ casado@uma.es)

University of Málaga <https://orcid.org/0000-0003-0373-1303>

Article

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Abstract

New insights on the mechanisms of spin relaxation and spin mobility in connection with the structural flexibility of π -conjugated radicals are fundamental solid-state issues in organic spintronics. Here, we describe a new azobenzene-based organic diradical with a dumbbell shape in the crystal and correlate its solid-state flexibility and its spin diradical structure. X-ray temperature-dependent studies were carried out showing two main effects on heating: i) modulation of the spin distribution and of the low-to-high spin magnetic transitions; and ii) “*normal*” quinoidal→aromatic transformation at low temperatures driven by the intramolecular rotational motions/mobility of the azobenzene core, and a “*reversed*” aromatic→quinoidal change at high temperatures activated by a bicycle pedal motion in the azobenzene unit amplified by anisotropic intermolecular interactions. Sequential versus simultaneous thermal excitation of the vibrational states associated to these motions reveal a unique and unprecedented spin-vibration mechanism.

Introduction

The spin is an intrinsic property of matter at the atomic world playing a decisive role in the physics of metals and semiconductors, and in the electro-optical properties of organic π -conjugated materials. In π -organics, the microscopic mechanisms of spin mobility/delocalization and spin-relaxation, such as hyperfine, spin-orbit or spin-lattice couplings, are poorly understood given their inherent weaknesses.^{1–3} On the way to uncover the fundamental properties of the spin in the organic matter, we here describe an interesting mechanism of spin-vibration coupling in a diradicaloid molecule realized by the confluence of three factors: i) a unique quinoidal/aromatic diradical structure, ii) the flexibility of the organic backbone and iii) the solid state crystal structure. Here, by first time, the new features of the molecular physics of diradicals are uncovered: i) thermal spin mobility in a diradical in connection with a mechanism of spin-vibration coupling, and ii) the unprecedented cohabitation of “normal” and “reversed” quinoidal→aromatic transformations on heating in a diradical.

Diradicals have always attracted attention of chemists owing to their unique role in understanding the fundamental nature of chemical bonds and of reactivity.^{4–9} In the last decade, the class of diradicals based on open-shell π -conjugated structures have become of interest in various organic electronic and magnetic applications.^{10–12}

The azobenzene has been shown to be a solid state building scaffold¹³ able to bringing intramolecular torsional mobility to their crystals consisting in non-translational displacements such as the so-called *bicycle pedal motion* associated to the inversion of the *NN* double bond orientation relative to the lateral benzenes, a unique feature first described in carotenoids (e.g., retinal)¹⁴ associated with the sequence of double and single bonds of the conjugated path (Scheme 1).

Pursuing to imprint the azobenzene moiety with magnetic activity, we here design a diradical molecule through a straightforward coupling reaction between azobenzene with two lateral phenoxyl units (**CAR** in

Scheme 1). The dual role of the azobenzene providing the electronic correlation between the two radicals and a flexible *NN* bridge produces a unique magnetic solid. **CAR** possesses a singlet diradical ground state and several thermal solid-state singlet-triplet excitation processes within 2 kcal mol⁻¹. This variety of energy transitions are promoted by intramolecular conformational mobility of the central azobenzene regarding the terminal “anchored” phenoxy sites. At the low temperature, heat absorption provokes the preferential excitation of low energy torsional modes of the “freer” azobenzene driving the π -conjugated structure towards a more aromatic form, or “normal” quinoidal→aromatic transformation. Surprisingly, this aromatic structure then steps back to a less diradical structure thanks to the additional thermal, likely intermolecularly cooperative, population of a molecular bicycle pedal motion that conducts further heat absorption and that produces a thermalized molecular structure with smaller diradical character, or “reversed” quinoidal→aromatic change. In consequence, a thermal modulation of the spin density distribution and spin mobility as a function of the temperature in the solid by torsional conformational mobility is described.

Results And Discussion

Thermal evolution of the crystal structures: bond distances and dihedral angles.

The detail of synthesis and characterization of **CARH** (non-diradical fully aromatic CAR analogue) and **CAR** were described (Supplementary Figs. 1–3). Single crystals of **CARH** and **CAR** were grown by using the slow solvent evaporation method in dichloromethane solution under N₂ atmosphere. The structure of **CAR** was studied at several temperatures with main focus in those at 130, 290 and 340 K. The average R factor of these structures is around 6.5%, which is reliable for the forthcoming discussion. The selected bond lengths for **CARH** and **CAR** are shown in Figs. 1 and 2 (Supplementary Fig. 4 and Tables 1–6).

The following structural features are highlighted. At 130 K, in Fig. 1: i) the two phenoxy substituents in **CARH** are twisted regarding the central azobenzene core with a dihedral angle of 38.76° whereas this angle is 5.78° in **CAR**; ii) the carbon-oxygen bond length in **CAR** (1.245 Å) is shorter than that in **CARH** (1.377 Å), which is very close to a typical carbon-oxygen double bond of *p*-terphenylquinone (1.231 Å)¹⁵; iii) a significant bond length alternation of r_2 , r_3 , r_4 in the two phenoxy benzenoid rings is observed; and iv) a crucial change of the nitrogen-nitrogen bond r_{10} length from 1.252 Å in **CARH** to 1.300 Å in **CAR**, indicating its partial nitrogen-nitrogen single bond character. All these features indicate a sort of *quinoidal-like* (hereafter, Q) structure on the phenoxy groups of **CAR** at 130 K.

At 290 K: i) the single crystal structure reveals that the nitrogen-nitrogen bond r_{10} (1.257 Å) becomes much closer to that of **CARH** (1.252 Å); ii) the bond length alternations of r_6 , r_7 , r_8 in the internal benzene rings become smaller; iii) the carbon-carbon bond r_5 (1.478 Å) in **CAR** is almost identical to that of **CARH** (1.484 Å); and iv) the carbon-oxygen r_1 and carbon-carbon bonds r_2 , r_3 , r_4 do not show significant changes at 290 K. These all suggest an exclusive transformation of the azobenzene core at 290 K attaining a structure closer to that typical of aromatic azobenzene. Overall, the bond length changes from

130 to 290 K are mainly in the azobenzene core documenting a decreasing quinoidal character in favor of a more *aromatic-like* shape (hereafter, A). This type of transformation is typically found in diradicals and can be termed as a “normal” quinoidal→aromatic step .

Surprisingly, the most significant changes at 340 K compared to 290 K are: i) the length of r_5 is 0.029 Å shorter than at 290 K (similar to that at 130 K); and ii) the r_7 CC bond length decreases by 0.024 Å becoming similar again to that at 130 K. This 290→340 K changes indicate the regaining of partial quinoid character at 340 K or *pseudo-quinoidal structure* (hereafter, PQ). In diradicals and in π -conjugated molecules, a continuum in the “normal” quinoidal→aromatic transformation is always observed on heating, what makes certainly unexpected this structural A→PQ inversion, a new and, to the best of our knowledge, unknown “reversed” quinoidal→aromatic transformation we discover in **CAR**.

The thermal variation of the dihedral angles in Fig. 2 (Supplementary Fig. 5) uncovers two distinctive effects. First, an *inter-ring torsional motion* as the temperature increases to 290 K in which dihedral angles between the connected phenoxyl and azobenzene rings vary: for instance, from 5.78° at 130 K to 8.96° at 290 K, and then a reduction up to 8.36° passing to 340 K. Second, the two terminal phenoxyls are twisted in opposite ways with respect to the central azobenzene thereby assuming the same absolute angle value but opposite signs. The simultaneous presence of the same terminal group twisted in opposite directions in the same molecule and crystal environment, at the same time associated with the opposite orientation of the N = N group suggests the active role of the *bicycle pedal motion* well known in crystals of azobenzene derivatives.¹³ This dihedral angle evolution delineates a combined effect of the pedal motion jointly acting with the phenoxyl twist owing to the existence of rotational mobility of the azobenzene core which is expected to increase with temperature. In line with this, the crystal structure also shows that the CCNN dihedral α , associated with the bicycle pedal motion of the two CC adjacent to the central NN, changes sign with temperature: although the value is always small, the sign change further corroborates the rotational mobility.

Physical properties. Magnetic susceptibility of solid **CAR** was measured using a Quantum Design MPMS 5XL SQUID magnetometer and a value of $-0.000295 \text{ emu mol}^{-1}$ was used as Pascal's correction¹⁶ for diamagnetism of the sample and holder (Supplementary Fig. 6). The plot of χT -T in Fig. 3a shows a curvilinear relationship, Furthermore, the χT value ($0.35 \text{ emu K mol}^{-1}$) of **CAR** at 300 K is smaller than the theoretical value of an ideal diradical ($0.75 \text{ emu K mol}^{-1}$) indicating antiferromagnetic coupling in the ground electronic state. By fitting the curves with a modified Bleaney-Bowers Eq. 1⁷, the single-triplet energy gap (ΔE_{ST}) amounted to $-1.31 \text{ kcal mol}^{-1}$

The ESR spectra (Fig. 3b) showed characteristic triplet patterns at 130 K arising from thermally populated triplets. These are: i) ESR resonances are split by the zero-field splitting; and ii) the unique half-field forbidden transition triplet signal ($\Delta m_s = \pm 2$) at 168 mT was observed at 130 K (Fig. 3a inset) which is rarely found in thermally excited triplets of organic singlet diradicals.¹⁸ The zero-field splitting parameters amount to $D = 0.00503 \text{ cm}^{-1}$ and $E = 0.00013 \text{ cm}^{-1}$ from the spectrum simulation. From the D value, the

average distance between the two triplet unpaired electrons ($D \sim 1/d^3$) was calculated as $d = 8.04 \text{ \AA}$, which is shorter than the length of azobenzene moiety ($9.094 \text{ \AA}$) suggesting that the spin density is mostly in the molecular center at 130 K in agreement with the remaining phenyls attaining a more quinoidal shape (Q form). Variable-temperature ESR measurements were also performed (Supplementary Fig. 7) and the ΔE_{ST} was estimated to be $-3.41 \text{ kcal mol}^{-1}$ by fitting the curves with the Bleaney-Bowers equation (Supplementary Fig. 8), which agrees with the SQUID result.

The solid-state optical absorption spectrum of **CAR** in Fig. 3c (Supplementary Fig. 9) shows two weak bands at 888 and 997 nm due to the $S_0 \rightarrow S_1$ transition to a dark double exciton state typically arising in diradicals.¹⁹ The strongest band owing to the $S_0 \rightarrow S_2$ excitation is at 645 nm. Figure 3d represents the Raman spectra of **CAR** taken with the Raman excitation laser lines at 633 nm (in resonance with the 645 nm absorption) and at 1064 nm (in pre-resonance with the 997 nm band). The two spectra share the bands at 1597 and 1563 cm^{-1} (blue shaded 1 and 2 bands in Fig. 3d) while the 1064 nm spectrum have additional bands at $1540 - 1530 \text{ cm}^{-1}$ (red 3 bands in Fig. 3d) which vibrationally identifies the double exciton state of the **CAR** diradical.

Singlet-triplet gaps (ΔE_{ST}) and thermal spin distribution. To further understand the magnetic structure of **CAR**, DFT calculations were carried out at B3LYP/6-31G(d) and M06-2X/6-311G(d) levels (Supplementary Tables S7 and S8).²⁰⁻²⁴ Considering **CAR** in isolated in the vacuum, an open-shell singlet ground state and a ΔE_{ST} gaps of $-0.43 \text{ kcal mol}^{-1}$ (M06-2X/6-311G(d)) and $-0.94 \text{ kcal mol}^{-1}$ (UB3LYP/6-31G(d)) are predicted. On the x-ray molecular structures at 130, 290 and 340 K, UB3LYP/6-31G(d) quantum chemical calculations predict, respectively, three different ΔE_{ST} values of -2.62 , -0.80 and $-1.20 \text{ kcal mol}^{-1}$ which, on average, yields a value of $-1.54 \text{ kcal mol}^{-1}$ very close to the $-1.31 \text{ kcal mol}^{-1}$ from SQUID measurements. Furthermore, a diradical character value of $y_0 = 0.93$ is estimated for the in vacuum broken-symmetry (BS) optimized structure (M06-2X/6-311G(d) level); whereas values of $y_0 = 0.81$, $y_0 = 0.92$ and $y_0 = 0.88$ were calculated for the crystal structures of **CAR** at 130, 290 and 340 K, respectively. This theoretical description indicates the modulation and tuning of the diradical character of **CAR** in its thermal forms referred as Q form ($y_0 = 0.81$), A form ($y_0 = 0.92$) and PQ form ($y_0 = 0.88$). Hence, **CAR** has three singlet-triplet excitation processes due to the progressive thermal conversion of its structure. Unfortunately, these three ΔE_{ST} gaps could not be resolved experimentally by SQUID magnetometry which overall detects one single process.

In the crystal structures at different temperatures, spin distributions were calculated (M06-2X/6-311G(d)) and selected spin population values of specific atoms shown in Fig. 4a (Supplementary Fig. 10 and Table 9). As the temperature increases from 130 to 290 K, the spin density decreases in the azobenzene core (Fig. 4b) and moderately increases in the phenoxyls. The most obvious change of spin density lies in the N atom which decreases from 0.174 to 0.081 from 130 to 290 K and concomitantly the spin density of the azobenzene core become very small. At 340 K, the integrated spin density of the N atoms and of the azobenzene unexpectedly increase. Correlating spin distribution and molecular structures, at 130 K

the Q form spreads out the spin density more or less uniformly over the whole skeleton of **CAR** (light blue circles and red lines in Fig. 4). The transformation into the A form at 290 K largely concentrates the spin density in the terminal phenoxyls (red circles and black lines in Fig. 4) while at 340 K, the PQ structure again redistributes the spin density towards the central moiety.

Mechanism of spin delocalization.

The paths of transformation among different spin-delocalized structures. The thermal transformation of **CAR** along the y_0 coordinate corresponds to two separated processes, an increase (0.81→0.92) for Q→A followed by a decrease (0.92→0.88) for A→PQ wherein the latter step cannot be viewed as a way back of the former. This is deduced from calculations of the Huang-Rhys factors²⁵ alongside the two above structural transitions (Supplementary Table 10) which reveal that the set of vibrational normal mode contributions that conduct the two transformations are different (e.g., there is not a vibrational reaction coordinate that sequentially transforms among them). Hence, the portion of the potential energy surface (PES) driving the structural changes of **CAR** may be figured out in a multidimensional space in which not only stretching coordinates but critically here torsional nuclear displacements, more likely affected by the solid-state environment, are involved. The multidimensional character of reaction coordinates of **CAR** agrees with the simultaneous changes observed experimentally for the π -bond distances and for the dihedral angles from x-ray data.

The effect of the crystal in the spin transformation: QM/MM calculations. Given the distinctive role of torsional motion, the PES of **CAR** was explored with QM/MM calculations (Supplementary Figs. 11, 12, 13 and 14) as a function of: i) the *inter-ring torsion* around the CC bonds connecting the azobenzene moiety with the phenoxyl terminal units (Fig. 5a), and ii) the *bicycle pedal motion* involving the two CC bonds adjacent to the central azo group (Fig. 5b). The three crystal geometries at 130, 290 and 340 K were considered inside a cluster formed by 18 molecules that completely surround the central one, described at QM level, to include the effects (via MM potential) of the nearby molecules in the crystal.

The simultaneous torsion of the two CC bonds may occur by twisting the whole azobenzene moiety inside the crystal cavity with respect to the terminal phenoxyls which remain almost positionally cleaved (dumbbell structure), such as drawn schematically in Fig. 5. Similarly, also the bicycle pedal motion in Fig. 5 can occur by leaving the terminal moieties of the **CAR** molecule almost fixed. We thus realize that these two motions are unique to jointly provide with torsional solid-state mobility to azobenzene.

A key point is that the QM/MM computed PES along the two Q→A and A→PQ selected torsional paths are asymmetric (Fig. 6 and Supplementary Fig. 12–14) with respect to the planar structure in contrast with the isolated/in vacuum computed PES which is symmetric with two degenerate energy minima separated by a small barrier (i.e., such as in biphenyl)²⁶. The asymmetry is more marked for the torsion of the whole azobenzene with respect to the phenoxyl groups (Fig. 6) compared to the bicycle pedal motion as determined by the interaction with neighbor molecules in the crystal, which are kept fixed while scanning the PES. The PESs alongside the 130 to 290 K transformation do not intercept each other by

varying the torsional angle (Supplementary Fig. 12) indicating that the Q→A transformation is progressive and might be driven by entropy effects based on the increase of molar entropy on going towards a more distorted structure. The increase of entropy is conducted by thermal excitation/population of low energy torsional modes which is not reflected in the PESs behavior.

The consideration of the 290 and 340 K PES's shows a crossing around 30 ° in which the A form is favored for $\theta > 30^\circ$ and the PQ form is preferred for $\theta < 30^\circ$. This crossing could be favored and modulated by coupling with the bicycle pedal motion. In fact, if we look at a **CAR** molecule inside the crystal, and focus on the two closest **CAR** molecules (above and below the central one in Supplementary Fig. 5), the θ angle is found positive or negative only when coupled with a specific orientation of the azo group. This suggests that the torsion of the azobenzene may be coupled with the bicycle pedal motion. Therefore, it is the joint action of the torsion of azobenzene and of the bicycle pedal motion that assists the crossing between PESs and drives the geometry change occurring with the temperature increase, such as schematized in Fig. 5. The A→PQ transition takes place as a way to reduce the interaction energy in a given interval of dihedrals.

Taking into account the distinctive out-of-plane topologies of the twisting and bicycle pedal motions, the observed transformations can be rationalized: i) the “normal” Q→A change is exclusively driven by low energy torsions which always favors the aromatic structures; however, ii) when the higher energy bicycle pedal vibrational states are excited together with the torsional vibrations, a less distorted thermalized molecular structure, PQ, with smaller diradical character is preferred, outlining a “reversed” quinoidal→aromatic transformation.

Conclusion

Here, we successfully synthesized and characterized a conjugated bis(phenyloxy) azobenzene diradical (**CAR**), which possesses a singlet open-shell ground electronic state. **CAR** has a solid-state magnetic structure consisting in the existence of several singlet-triplet thermal excitations accompanied by a thermal tuning of the spin mobility. **CAR** displays such solid-state modulation thanks to the intramolecular mobility/flexibility imprinted here by the azobenzene moiety due to the dumbbell structure of **CAR**. These magnetic processes involve three structures, all with large diradical character: a quinoidal-like form ($y_0 = 0.81$) at low temperature, an aromatic-like form ($y_0 = 0.92$) at intermediate values and a pseudoquinoidal-like form ($y_0 = 0.88$) at high temperatures. These transitions are progressive and driven by the population of torsional modes coupled with the bicycle pedal torsional motion of azobenzene. Distinctively, whereas heating at low temperatures produces a “normal” Q→A step, the case of the “reversed” quinoidal→aromatic transformation, or A→PQ, aromatic→pseudoquinoidal transformation is conducted by the torsional/bicycle pedal modes causing a lowering of the total interaction energy at small dihedral angles thus favoring a more planar pseudoquinoidal form. These two processes highlight mechanisms of single (torsions) and double-coupled (torsions plus bicycle pedal) electron-vibration couplings which imparts such a unprecedented thermal spin mobility in the **CAR** diradical.

Methods

Synthesis. CARH was readily synthesized using 4,4'-dibromoazobenzene and 2,6-di-*tert*-butylphenoxy substituents under a typical Suzuki-Miyaura cross-coupling reaction condition with Pd(PPh₃)₄ as catalyst and Na₂CO₃ as base in THF solution. Subsequently, when treated with excess lead (IV) oxide in dichloromethane CARH was easily oxidized to **CAR** in high yield (see supporting information).

DFT calculations. All calculations were performed with the Gaussian 16 program suite. For isolated CAR molecules we used Density functional theory (DFT) with M06-2X exchange-correlational functionals and employed the 6-311G(d) basis set for all atoms. Additional calculations, including Huang-Rhys parameters were carried out using B3LYP functionals and the 6-31G* basis set. Full geometry optimizations were carried out at the (U)M06-2X/6-311G(d), B3LYP/6-31G* levels, and the obtained stationary points were characterized by frequency calculations. The spin correction for singlet-triplet energy gap was calculated using Yamaguchi's procedure which includes the energy difference between BS singlet and open-shell triplet and the correction for spin contamination. QM/MM calculations were performed with the ONIOM model, using the B3LYP functional and 6-31G* basis set for the high-level region (i.e. central **CAR** molecule) and the QM calculations included electronic embedding. The low-level region (molecular mechanics) was modelled by atomic point charges determined by the Qeq approach using the Dreiding force field parameters attributed to the fixed molecular geometry of the surrounding **CAR** molecules.

Data availability. Data supporting the findings of this study are available within the article and its Supplementary Information files. Crystallographic data for CARH and CAR can be obtained from the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk) by CCDC-2006244(CARH), CCDC-2006243(CAR 130K), CCDC-2006239(CAR 200K), CCDC-2006240(CAR 250K), CCDC-2006241(CAR 290K) and CCDC-2006242(CAR 340K). The authors declare that all other data supporting the findings of this study are available within the paper [and its supplementary information files].

Declarations

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Author contributions

Y.S. conceived the project, and designed and carried out the experiments. F.M. analyzed the data and wrote the manuscript. Y.H.Z. conceived the project and played a critical role in discussions of the experimental design, project direction, experiments and results, and preparation of the manuscript. H.J.C. carried out and analyzed the SQUID and ESR magnetic measurements. G.D.X calculated and analyzed the spin density distribution. S. M.Q. and J.C. performed the Raman spectroscopic measurements. Y.D. and F.N. performed the calculations and analyzed the data from these computations. J.C. and F.N. provided the mechanism of spin vibrational coupling and discussed it in the context of the experimental results. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Scheme

Scheme 1 is available in the Supplemental Files section

Figures

Figure 1

Temperature-dependent single crystal structures of CAR. (a) Single-crystal X-ray structures with selected bond lengths of CAR at 130, 290 and 340 K with thermal ellipsoids at the 50% probability level. H atoms are not shown for clarity. (b) Selected bond lengths (Å) values of CARH and CAR.

Figure 2

Dihedral angles of CAR at different temperatures. The dihedral angles involved in the twisting of phenoxy rings and in the bicycle pedal motion of the central azo group of CAR together with the values of these angles as a function of the temperature.

Figure 3

Solid-state magnetic and spectroscopic properties of CAR. (a) Temperature-dependent plots of χT versus T and fitted χT -T curve (solid line) for CAR measured at 1.0 T from 2 to 300 K. The half-field transitions ($\Delta m_s = \pm 2$) are shown as insets. (b) ESR spectra of 1 mmol L-1 CAR in a frozen glass (toluene) at 130 K. (c) UV-Vis-NIR electronic absorption spectrum in solid state of CAR at room temperature; (d) Room temperature solid state Raman spectra of CAR taken with the 633 nm and 1064 nm excitation laser lines.

Figure 4

Spin density distribution of CAR. (a) Selected bond lengths and calculated spin population at certain atoms of CAR at different temperatures. (b) The integral spin density changes of phenoxyl and azobenzene moieties at temperatures of 130, 200, 250, 290 and 340 K.

Figure 5

Sequential vs Simultaneous action of torsion and bicycle pedal motions. Simulations (not at scale) of the dihedral torsion motion of the azobenzene relative to the phenoxyls provoking the Q→A transformation (top, a) and of the combined torsional plus bicycle pedal motions of the central azobenzene moiety provoking the A→PQ transformation (bottom, b).

Figure 6

Potential energy surface dependence of CAR with torsion and bicycle pedal motions. Left: torsional angle potential energy profiles of the CAR molecule inside the crystal structure at 290 K (A form) and of that at 340 K (PQ form). Right: potential energy profiles of the CAR molecule inside the crystal structure at 290 K (A form) and of that at 340 K (PQ form) alongside the bicycle pedal motion distortion. Calculations were carried out with the QM/MM ONIOM model on the cluster of CAR molecules, B3LYP/6-31G* level with electronic embedding for the central molecule, Dreiding force field and charges determined with the Qeq approach for the MM part.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

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- [SY290K0m.cif](#)
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