Transannular interaction in 4,7-[2.2]paracyclophane quinone

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The molecular and crystal structure of 4,7-[2.2]paracyclophane quinone and its thermal motion have been studied using single-crystal X-ray diffraction data. Topological analysis of the electron density distribution [MP2(FC)/6-31G(*d*,*p*) calculation] revealed the absence of intramolecular transannular interactions between two aromatic rings.

The [2.2]paracyclophane (PCP) derivatives are of great interest as potential optoelectronic and non-linear optic materials.[1] Their properties depend on the presence of two closely spaced and conformationally defined aromatic rings, which are responsible for intramolecular charge transfer. In spite of the π–π* electron transitions in some PCP derivatives[2] (the indication of the transannular interaction in the excited state), the possibility of this interaction in the ground state of PCP is practically not studied yet.

Recently, X-ray diffraction and quantum-chemical [MP2(FC)/6-31G(*d*,*p*)] topological analysis of the electron density distribution function $\rho(r)$ in unsubstituted PCP have revealed the absence of transannular interactions in the ground state despite of a shortened distance between aromatic desks and the presence of this interaction in the excited state.[3]

In order to evaluate the influence of the nature of aromatic rings on the electron density characteristics of paracyclophanes, 4,7-[2.2]paracyclophane quinone (PCPQ) has been studied. PCPQ is of interest because the aromatic desks are nonequivalent. Semi-empirical quantum-chemical (CNDO/S) data also indicate that intramolecular charge transfer takes place in both the ground and excited states of this molecule.[2(*b*)] Taking into account that the calculations were performed for a model geometry with an interring separation of 3.2 Å, we performed X-ray diffraction analysis and a quantum-chemical study of this compound to obtain information on the geometrical and electronic structure of PCPQ.

The heterochiral crystal of PCPQ was previously studied,[4] and a static disorder (superposition of enantiomers) was found in this crystal (space group *C*2/*c*). In this work, a homochiral crystal[5] of the *R*-enantiomer was studied using X-ray diffraction analysis.[†]

The geometry analysis of PCPQ demonstrated that the principal bond lengths and bond angles are similar to the corresponding values in [2.2]paracyclophane[3] (Figure 1). The quinone ring (A) is characterised by a boat conformation with the deviation of the C(3) and C(6) atoms by ~0.215 Å. The conformation of an unsubstituted ring (B) is also boat with the deviation of the C(11) and C(14) atoms by 0.136 Å, which is slightly smaller in comparison with that in unsubstituted PCP (0.156 Å). It is noteworthy that in spite of this difference the ethylene bridge bond lengths in PCP and PCPQ are equal (1.578 Å). This results in a decrease of the distance between boat 'bases' from 3.099 Å in PCP to 3.048 Å in PCPQ. The bond lengths in aromatic rings A and B alternate and actually do not differ from the corresponding values in the unsubstituted quinone[5] and PCP (Figure 1).

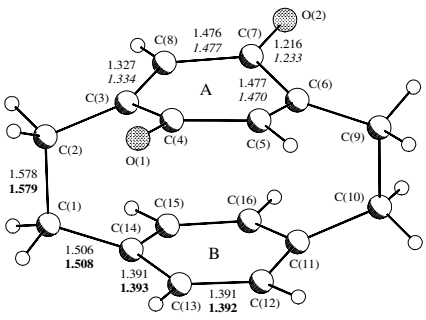

Figure 1 Bond lengths (Å) in PCPQ, PCP (bold faced) and quinone (italics). The values are given with the account of C_2 molecular symmetry (the experimental values are averaged).

The main distinctive feature of the PCP structure is the twist conformation of ethylene bridges with the pseudo-torsion angle C(1)C(2)C(9)C(10) (φ) equal to 11.4°. Note that the φ angle in paracyclophane derivatives varies in a wide range, and in unsubstituted PCP the φ angle decreases from ~3 to 0° upon cooling a crystal from 298 to 100 K due to a dynamic disorder in the crystal.[3,7]

A similar trend was also observed in the crystal of PCPQ, although its cooling down to 110 K did not resolve the disorder. The presence of a residual disorder in the PCPQ molecule was found during the analysis of atomic anisotropic displacement parameters in the framework of the LTS rigid-body model[8] (calculations were carried out with the THMA-11 program[9]). In particular, an analysis of the mean-square displacement amplitudes (Δ)[10] demonstrated that although all C–C bonds satisfy the Hirshfeld rigid-bond criteria ($\Delta = 1–16\times10^{-4}$ Å^2), similar Δ values for some of C···C intramolecular contacts between the rings exceeded 100×10^{-4} Å^2. This is the direct indication of the mutual parallel motion of the rings in the PCPQ molecule in a crystal.

Such a type of disordering in PCPQ excludes the possibility of the experimental analysis of $\rho(r)$ in the crystal. Therefore, the electronic structure and the transannular interaction in PCPQ were analysed on the basis of the *ab initio* MP2(FC)/6-31G(*d*) calculation.

† *Crystallographic data for PCPQ*: at 110 K, crystals of $C_{16}H_{14}O_2$ are tetragonal, space group $P4_12_12$, $a = 11.2757(2)$ Å, $c = 18.394(3)$ Å, $V = 2338.6(3)$ Å^3, $Z = 8$, $M = 238.27$, $d_{calc} = 1.353$ g cm^{-3}, μ(MoKα) = 0.88 cm^{-1}, $F(000) = 1008$. Intensities of 3879 reflections were measured with a Smart 1000 CCD diffractometer at 110 K [λ(MoKα) = 0.71072 Å, ω-scans with a 0.3° step in ω and 20 s per frame exposure, $2\theta < 60°$], and 3408 independent reflections ($R_{int} = 0.0128$) were used in further refinement. The structure was solved by a direct method and refined by the full-matrix least-squares technique against F^2 in the anisotropic–isotropic approximation. Hydrogen atoms were located from the Fourier synthesis and refined in the isotropic approximation. The refinement converged to $wR_2 = 0.1660$ and GOF = 1.040 for all independent reflections [$R_1 = 0.0653$ was calculated against F for 2339 observed reflections with $I > 2\sigma(I)$]. All calculations were performed using SHELXTL PLUS 5.0 on IBM PC AT.

Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge *via* www.ccdc.cam.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 204622. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2003.

The *ab initio* calculations were performed with the Gaussian-98 program package[13] at the MP2 level. Full optimization with the C_2 symmetry of the molecule was carried out with the 6-31G(*d*) basis set starting from the X-ray geometry data. As the convergence criteria, the default threshold limits 0.00045 and 0.0018 au were applied for the maximum force and displacement, respectively. Topological analysis of the $\rho(r)$ function (AIMPACK[14]) was based on the wave functions obtained by MP2 calculations.

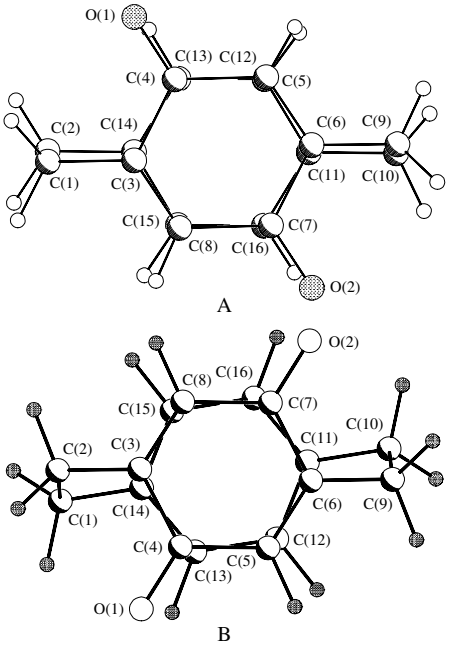

Figure 2 General view of PCPQ in a crystal (A) and an isolated state (B). Selected bond lengths (Å) obtained from the MP2(FC)/6-31G(*d*) calculation: C(1)–C(2) 1.577, C(2)–C(3) 1.500, C(3)–C(4) 1.487, C(4)–C(5) 1.477, C(5)–C(6) 1.355, C(4)–O(1) 1.239; the interplane distance is 3.011 Å.

The calculated geometrical parameters of PCPQ within the chosen level of theory and basis set are in an excellent agreement with the experimental data with the only one exception of the mutual orientation of the rings. Thus, in the isolated state, the pseudotorsion angle φ is 38° (11.4° in the crystal). In addition, the arrangement of the rings in the isolated state is not 'eclipsed' as in the crystal but 'staggered' with the turn angle equal to 9° (Figure 2). The variation of the mutual orientation of rings is accompanied by a shortening of the interplane distance down to 3.011 Å (3.048 Å in the crystal). Taking into account the flexibility of PCPQ, it seems that the above difference in the mutual arrangement of the rings arises due to the presence of the C–H···O interaction of a moderate strength [C(12)–H(12)···O(2) $(-1/2 + x, 1/2 - y, 1/4 - z)$ C(12)···O(2) 2.320(3) Å, C(12)H(12)O(2) 167°].

To investigate the nature of intramolecular interactions in PCPQ, topological analysis of the electron density distribution in terms of the 'Atoms in Molecules' (AIM)[11] theory was carried out. Taking into consideration the nonequivalence of rings in PCPQ, it was possible to expect that a decrease of the intramolecular C···C contacts between the π-donor and π-acceptor rings is a consequence of the through-space charger transfer. In terms of the AIM theory, this suggests the presence of the critical points (3, –1) of the $\rho(r)$ in the intramolecular space.[11]

However, topological analysis of the charge distribution in PCPQ revealed that a characteristic set of the critical points (CP) in 4,7-[2.2]paracyclophane quinone is identical to the corresponding one in unsubstituted PCP. All CPs (3, –1) are localised at the C–C, C–H and C=O bonds, while in the intraring area only critical points (3, +3) and (3, +1) corresponding to the formation of a cage and 11-membered rings, respectively, were found (Figure 3).

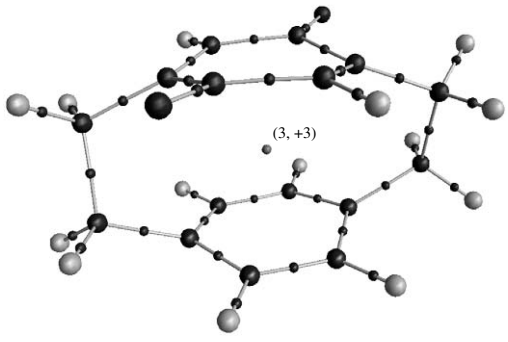

Figure 3 Critical points (small spheres) and bond paths in PCPQ according to the MP2(FC)/6-31G(*d*) calculation. Points (3, +1) are omitted for clarity.

Note that the topological characteristics of $\rho(r)$ [values of $\rho(r)$, $\nabla^2\rho(r)$, bond ellipticity and local energy densities] in the critical points (3, –1) of the phenyl ring coincide with the corresponding values in unsubstituted paracyclophane. The main differences between PCPQ and PCP are observed for CP (3, +1) of the phenyl ring and the absolute value of λ_1 eigenvalue of the Hessian matrix ($|\lambda_1|$), which corresponds to the curvature of electron density distribution in the direction perpendicular to the ring plane.[12] The decrease of $|\lambda_1|$ in PCPQ (0.27 eÅ^{-5}) in comparison to PCP (0.37 eÅ^{-5}) is an indication of additional charge density accumulation between phenyl and quinone ring planes, which is consistent with an increase in the $\rho(r)$ value in the cage CP (3, +3) (0.03 and 0.04 eÅ^{-3} in PCP and PCPQ, respectively).

Thus, despite of the presence of the π-donor and π-acceptor rings, and an increase of the charge density within 4,7-[2.2]paracyclophane, the transannular interaction is still absent. Hence, charge transfer in the excited state[2(*b*)] cannot be considered as a sufficient criterion of the presence of intramolecular charge transfer in the ground state of paracyclophanes without a detailed analysis of their electron density function.

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