The role of intermolecular H⋯H and C⋯H interactions in the ordering of [2.2]paracyclophane at 100 K: estimation of the sublimation energy from the experimental electron density function

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The intermolecular interactions responsible for the ordering of the [2.2]paracyclophane molecule in a crystal at 100 K have been found out and their strengths and the lattice energy have been estimated on the basis of a high resolution X-ray diffraction study and plane-wave DFT calculations.

Among macroscopic properties, the heat of sublimation (ΔH_{subl}) of a compound is most interesting for an analysis of intermolecular forces responsible for crystal formation.[1] Using a simple partition division of the sublimation energy by the number of intermolecular contacts, one can obtain the exact or average value of their energy.[2,3] This approach has a definite benefit: the energy of an interaction of interest is defined in the bulk what is significant in most cases, but also has some restriction: the

researcher must know the number of contacts, which correspond to attractive interactions. In addition, such a scheme can be used only if all contacts in a crystal are of the same type.

The value of ΔH_{subl} is closely related to the lattice energy,[1] which can be obtained with high accuracy using periodic quantum-chemical calculations within the plane-wave density functional theory (PW-DFT), as it was recently demonstrated for the crystals of ammonia,[2] urea[2] and BH_3–NH_3.[3] In turn, it made possible the estimation of the energy of N–H···O, N–H···NH and B–H···H–N bonds in solids.[2,3]

On the other hand, the energy of intermolecular interactions and thus the lattice energy can be estimated from the topological analysis of the electron density distribution function $\rho(r)$ in a crystal within Bader's 'Atoms in Molecule' theory.[4] The latter possibility is based on the found correlation between the energy of the contact (E_{cont}) with the value of the potential energy density function $v(r)$ in the corresponding critical point $(3, -1)$.[5] While this approach is much more complicated than PW-DFT, it clearly overcomes the above problems and can be used for the estimation of energy of any type and number of inter- and intramolecular interactions and thus can also be used for the estimation of the sublimation energy. For example, within the experimental and theoretical analysis of the $\rho(r)$ in the crystal of 1-phenyl-*o*-carborane, it was shown that X–H···H–X (X = C, B) intermolecular contacts correspond to attractive interactions and play a dominating role in the formation of the crystal structure.[6] The total energy of the H···H contacts per independent molecule (68.6 kJ mol^{-1}) is close to that obtained within the PW-DFT calculation of the crystal (71.1 kJ mol^{-1}).[6]

We have performed an experimental X-ray diffraction (XRD) study and a PW-DFT investigation of crystal packing in [2.2]para-cyclophane (pCp). The crystal packing of pCp significantly influences the molecular symmetry. The XRD analysis of pCp at room temperature has shown that the maximum molecular D_{2h} (*mmm*) symmetry (space group $P4_2/mnm$) was not fulfilled in the crystal and resulted from the superposition of two equal twisted conformations with the C(1)C(1B)C(1C)C(1A) twist angle of 3° (see Figure 1 for atom numerations).[7] In contrast, an analysis of anisotropic displacement parameters (ADPs) at 100 K has revealed that the molecule is ordered with the highest D_{2h} symmetry.[8] The problem of the molecular symmetry of pCp for an isolated molecule has been considered in recent publications.[8,9]

In order to find out which intermolecular contacts are responsible for the ordering of pCp at 100 K and to estimate their contribution to the lattice energy, we performed a topological analysis of the $\rho(r)$ function derived from the X-ray diffraction data at 100 K and refined it using a multipole model.[†] Additional information on the total energy of interactions in the crystal, as well as the molecular symmetry of pCp in the crystal, have been obtained within the PW-DFT (HCTH/120 functional) calculations.[‡]

Our results show that according to the PW-HCTH/120 calculation and in agreement with XRD at 100 K, the molecule
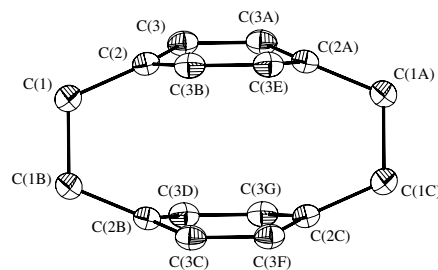

Figure 1 The general view of pCp at 100 K with the representation of atoms by thermal ellipsoids at a 50% probability level. The bond lengths according to XRD/PW-HCTH/120 (Å): C(1)–C(B) 1.580(1)/1.602, C(1)–C(2) 1.508(1)/1.506, C(2)–C(3) 1.400(1)/1.400, C(3)–C(3A) 1.392(1)/1.393, C(2)···C(2B) 2.786(1)/2.814, C(3)···C(3D) 3.099/3.129; deviation of the C(2) atom from the C(3)C(3A)C(3B)C(3E) plane is equal to 0.156/0.158 Å.

of pCp is characterised by ideal D_{2h} symmetry. The geometry of pCp according to PW-HCTH/120 calculation is close to experimental one with the only exception for the C–C bond lengths in the ethylene bridges (Figure 1). Although an elongation of this bond is a general feature of DFT calculations,[8] the C(1)–C(1B) bond length in the crystal, according to PW-HCTH/120, is only 1.602 Å against 1.614 Å in the isolated molecule.[8] This value according to XRD at 100 K is 1.580(1) Å. Thus, we can propose that the difference in the C(1)–C(1B) bond length in the isolated molecule and the crystal and, consequently, an increase in the interatomic distance between aromatics decks in an isolated molecule of pCp partly resulted from crystal packing effects.

In order to estimate the lattice energy per molecule in the crystal of pCp, we carried out additional PW-HCTH/120 calculations deleting all but one molecule from the crystal lattice thus creating a pseudo-isolated molecule. Taking into account that in both calculations the same basis set and level of theory were used, a comparison of energies for the crystal and isolated molecule gives the energy of the intermolecular interactions, which is equal to 95.96 kJ mol^{-1} for pCp. This value is close to the experimental ΔH_{subl}^0, which is equal to 96.2±4.2 kJ mol^{-1}.[10]

An analysis of the crystal packing of pCp has revealed that there are only two types of interatomic interactions, namely, H···H and H···C (Figure 2). Despite the presence of aromatic rings, the C···C interactions are not present.

Taking into account that all these contacts significantly exceed the sum of van der Waals radii and that only one of them [H(2)···C(3)] is characterised by pronounced directionality

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[†] The multipole refinement was carried out within the Hansen-Coppens formalism[11(a)] using the XD program package[11(b)] with the core and valence electron density derived from wave functions fitted to a relativistic Dirac-Fock solution.[11(c)] Before the refinement, the C(1)–H(2) and C(2)–H(1) bond distances were normalised to 1.082 and 1.094 Å in accordance with PW-HCTH/120 calculations. The level of multipole expansion was octopole for carbons or dipole for hydrogens. The refinement was carried out against F. The multipole refinement converged to R = 0.0211, wR = 0.0218 and GOF = 0.98 for 860 merged reflections with $F > 3\sigma(F)$. All bonded pairs of atoms satisfy the Hirshfeld rigid-bond criteria[11(d)] (difference of the mean square displacement amplitudes along the bonds did not exceed 8×10^{-4} Å^2). The residual electron density was no more than 0.08 eÅ^{-3}. Analysis of the topology of $\rho(r)$ functions was carried out using the WINXPRO program package.[12] The values of the potential energy density $v(r)$ were evaluated through the semiqualitative approximation[5(a)] for the kinetic energy density function $g(r)$ proposed by Kirzhnits.[13] The $g(r)$ function is described as $(3/10)(3\pi^2)^{2/3}[\rho(r)]^{5/3} + (1/72)|\nabla\rho(r)|^2/\rho(r) + 1/6\nabla^2\rho(r)$, which in conjunction with the virial theorem $2g(r)+v(r) = 1/4\nabla^2\rho(r)$ leads to the expression for potential energy density $v(r)$.

[‡] The quantum chemical calculations have been carried out using the CPMD 3.9.1 density functional (DFT) code.[14] For the optimization of atomic positions (started from an experimental crystal structure) in the crystal, a simulated annealing technique was used followed by BFGS minimization of the total energy. Non-local norm-conserving Troulier–Martins pseudopotentials[15] have been applied to account of core electrons while valence electrons were approximated by plane-wave expansion with 70 Ry cutoff in Kleinmann–Bylander decomposition.[16] Exchange and correlations terms of total energy were described by the HCTH/120 functional.[17] Kohn-Sham equations were integrated using a 4×4×4 Monkhorst–Pack k-point mesh.[18] Since DFT does not take into account dispersion interactions, calculated unit cell parameters may be systematically overestimated or underestimated up to 5%. Therefore, the experimental values of unit cell parameters were used in calculations. Atomic displacements converged better than 10^{-4} a.u., as well as energy variations were less than 1×10^{-6} a.u.

The isolated molecules were simulated utilising the same theoretical background, basis sets and convergence criteria by quantum chemical calculations of a single molecule in a cubic box with side of 15 Å. The structures of isolated molecules were tested on stability by calculation of vibrational frequencies and no negative ones were obtained. Unfortunately, the exact calculation of vibrational frequencies in case of periodic boundary conditions is difficult due to large requirements of computer time. Because of these difficulties, no zero point correction was applied to the sublimation energy. On the other hand, a plane wave basis set has no superposition error in contrast to an ordinary gaussian basis sets. We believe that the sublimation energy obtained may be successfully used as a valuable criterion for the characterization of the strength of intermolecular interactions in a crystal.
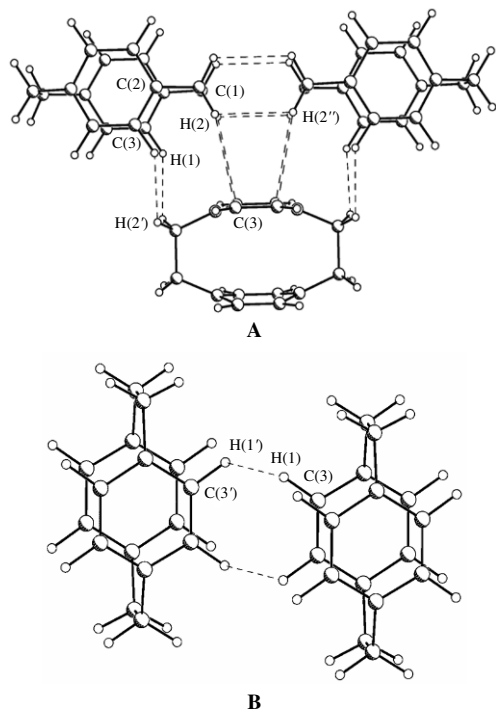
A

B

Figure 2 The fragments of the crystal packing of pCp illustrating the H···H and H···C contacts found according to a topological analysis of $\rho(r)$ in the crystal. The parameters of contacts in the pCp crystal according to XRD/PW-HCTH/120 (Å): H(1)···H(2′) 2.30/2.27, H(2)···H(2″) 2.60/2.52, H(2)···C(3) 3.058/3.221, H(1)···H(1′) 2.74/2.66 Å.

[C(1)H(2)···C(3) angle is equal to 155°], we performed a topological analysis of the $\rho(r)$ function according to X-ray diffraction data.

Since the detailed analysis of the electron density distribution within the pCp molecule in a crystal and an isolated state has been recently reported,[8] we focus our attention on intermolecular contacts. The critical point (CP) search has revealed that CPs (3, –1) are observed for five independent contacts: [H(1)···H(2′), H(2)···H(2″), H(2)···C(3), H(1)···H(1′)]. The geometrical parameters of these contacts in the crystal, according to XRD and PW-HCTH/120 calculations are close to each other and thus we can expect that their contribution to the lattice energy in real and calculated crystal could be approximately the same.

Among the contacts characterised by the presence of CP (3, –1), which can be considered as attractive interactions, there are three contacts in which the H(2) atom of the ethylene bridge participates. Although all of them as well as all others are rather weak [the values of $\rho(r)$ and $\nabla^2\rho(r)$ functions vary in the ranges 0.015–0.034 eÅ^{-3} and 0.30–0.43 eÅ^{-5}, respectively], they can influence the twisting motion in pCp.

Indeed, the energy of individual interactions is also small and equal to 2.0–3.25 or 1.50 kJ mol^{-1} for H···H and H···C contacts, respectively. However, the total energy of interactions for one ethylene bridge [four H(2)···H(2″), four H(2)···H(1′) and four H(2)···C(3) contacts] will be as high as 26.9 kJ mol^{-1}. Taking into account that the twist motion in pCp is practically barrierless, the observed total energy of contacts formed by the hydrogen atoms of the ethylene bridge with high probability leads to the ordering of the pCp core.

In turn, the increase of the unit cell dimensions at room temperature in the case of D_{2h} symmetry will cause a consequent elongation of each of H(2)···H(1)/H(2) and H(2)···C(2) contacts by approximately 0.035 and 0.2 Å, respectively, thus leading to the disorder of the ethylene bridge.

The total energy of all H···H and H···C contacts (32 contacts of the H···H type and 12 of the C···H type) per pCp molecule in the crystal is equal to 91.8 kJ mol^{-1}. Taking into account that both a topological analysis of the $\rho(r)$ according to XRD and PW-HCTH/120 calculations lead to lattice energies close to an experimental sublimation enthalpy, we can conclude that the

number and energy of the contacts found within XRD investigation is reliable.

Thus, high-resolution XRD investigations of electron density can be used for an analysis of crystal packings, and they allow us to distinguish and estimate the energy of all attractive interactions in the crystal what in the case of the [2.2]paracyclophane gives an opportunity to explain the dynamic behaviour of this molecule in a crystal.

References

1 (*a*) A. J. Pertsin and A. I. Kitaigorodsky, *The Atom–Atom Potential Method*, Springer Verlag, Berlin, 1986; (*b*) A. Gavezzotti, *J. Am. Chem. Soc.*, 1989, **111**, 1835; (*c*) A. Gavezzotti, *J. Phys. Chem.*, 1991, **95**, 8948; (*d*) A. Gavezzotti and G. Filippini, *Acta Crystallogr.*, 1992, **B48**, 537; (*e*) A. Gavezzotti and G. Filippini, *J. Phys. Chem.*, 1994, **98**, 4831.
2 C. A. Morrison and M. M. Siddick, *Chem. Eur. J.*, 2003, **9**, 628.
3 C. A. Morrison and M. M. Siddick, *Angew. Chem., Int. Ed. Engl.*, 2004, **43**, 4780.
4 (*a*) T. S. Koritsanszky and P. Coppens, *Chem. Rev.*, 2001, **101**, 1583; (*b*) R. F. W. Bader, *Atoms in Molecules. A Quantum Theory*, Clarendon Press, Oxford, 1990.
5 (*a*) E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Lett.*, 1998, **285**, 170; (*b*) Yu. A. Abramov, *Acta Crystallogr.*, 1997, **A53**, 264; (*c*) E. Espinosa, I. Alkorta, I. Rozas, J. Elguero and E. Molins, *Chem. Phys. Lett.*, 2001, **336**, 457; (*d*) V. G. Tsirelson, *Acta Crystallogr.*, 2002, **B58**, 632.
6 I. V. Glukhov, K. A. Lyssenko, A. A. Korlyukov and M. Yu. Antipin, *Izv. Akad. Nauk, Ser. Khim.*, 2005, in press.
7 H. Hope, J. Bernstein and K. N. Trueblood, *Acta Crystallogr.*, 1972, **B28**, 1733.
8 K. A. Lyssenko, M. Yu. Antipin and D. Yu. Antonov, *ChemPhysChem*, 2003, **8**, 817.
9 (*a*) S. E. Walden and D. T. Glatzhofer, *J. Phys. Chem. A*, 1997, **101**, 8233; (*b*) D. Henseler and G. Honeicher, *J. Phys. Chem. A*, 1998, **102**, 10828; (*c*) D. Henseler and G. Honeicher, *J. Mol. Struct. (Theochem)*, 2000, **497**, 145.
10 (*a*) D. L. Rodgers, E. F. Westrum, Jr. and J. T. S. Andrews, *J. Chem. Thermodyn.*, 1973, **5**, 733; (*b*) R. H. Boyd, *Tetrahedron*, 1966, **22**, 119.
11 (*a*) N. K. Hansen and P. Coppens, *Acta Crystallogr.*, 1978, **A34**, 909; (*b*) T. S. Koritsansky, S. T. Howard, T. Richter, P. Macchi, A. Volkov, C. Gatti, P. R. Mallinson, L. J. Farrugia, Z. Su and N. K. Hansen, *XD – A Computer Program Package for Multipole Refinement and Topological Analysis of Charge Densities from Diffraction Data*, 2003; (*c*) Z. Su and N. K. Hansen, *Acta Crystallogr.*, 1998, **A54**, 646; (*d*) F. L. Hirshfeld, *Acta Crystallogr.*, 1976, **A32**, 239.
12 (*a*) A. Stash and V. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371; (*b*) A. Stash and V. Tsirelson, *WinXPRO – a Program for Calculation of the Crystal and Molecular Properties Using the Model Electron Density*, Moscow, 2001. A further information available at http://xray.nifhi.ru/wxp/.
13 D. A. Kirzhnits, *Sov. Phys. JETP*, 1957, **5**, 64.
14 J. Hutter, P. Ballone, M. Bernasconi, P. Focher, E. Fois, S. Goedecker, M. Parrinello and M. Tuckerman, *CPMD v. 3.9.1, MPI für Festkorperforschung and IBM*, Zurich Research Laboratory, 1995–2004.
15 N. Troullier and J. L. Martins, *Phys. Rev.*, 1991, **B43**, 1993.
16 L. Kleinman and D. M. Bylander, *Phys. Rev. Lett.*, 1982, **48**, 1425.
17 A. D. Boese, N. L. Doltsinis, N. C. Handy and M. Sprik, *J. Chem. Phys.*, 2000, **112**, 1670.
18 H. J. Monkhorst and D. Pack, *Phys. Rev.*, 1975, **B13**, 5188.

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