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4,4-Diphenyl-2,5-cyclohexadienone: Four Polymorphs and Nineteen Crystallographically Independent Molecular Conformations[**]

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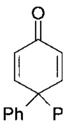
Polymorphism is the existence of the same chemical substance in at least two different crystalline arrangements of molecules.[1] The existence of polymorphism implies that free energy differences between different crystalline forms are small (1–2 kcal mol^{-1}) and that kinetic factors are important during crystal nucleation and growth.[2] Molecular conformations, packing arrangements, hydrogen bond synthons, and lattice energies of the same molecule in different crystalline environments can be compared in polymorphic structures. Polymorphs represent special situations for the study of structure–property relationships with a minimum number of variables, since differences arise from crystal packing effects and not because of the presence of a different chemical species. A proper understanding of polymorphism is important in crystal engineering[3] because the unexpected occurrence of a new polymorph can well demolish the best of crystal design strategies. Getting the correct polymorph[4] is of the utmost importance in the synthesis of drugs, pharmaceuticals, explosives, dyes, pigments, flavors, and confectionery products.



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We describe here four X-ray crystal structures of 4,4-diphenyl-2,5-cyclohexadienone (**1**) that exhibit conformational polymorphism,[5] conformational isomorphism,[5] and concomitant polymorphism[6]

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[**] A.N. thanks the DST, India, for research funding (SP/S1/G-29/98). We thank the Indo–UK bilateral cooperation project (INT/UK/P-15/99) of the DST and the British Council. V.S.S.K. thanks the CSIR, India, for a fellowship. The EPSRC, UK, is thanked for funding C.K.B and for a Senior Research Fellowship to J.A.K.H., and the ORS, UK, is thanked for supporting R.M. We thank Prof. G. R. Desiraju (Hyderabad) for discussions and suggestions.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

in the same system. While there are examples wherein only one of these phenomena occurs for a particular molecule,[7] their simultaneous occurrence for the same molecule is rare.[8] Initially, crystallization of **1** from EtOAc/hexane appeared to afford two concomitant polymorphs as characterized by single-crystal X-ray diffraction: a monoclinic form **A** in space group $P2_1$ ($Z = 2$) and a triclinic form **B** with four molecules in the asymmetric unit ($P\bar{1}$, $Z = 8$).[9] When data were collected on another crystal, a large triclinic cell ($P\bar{1}$, $Z = 24$, form **C**) was indexed[10] that could not be refined to better than $R = 0.11$ despite a satisfactory data/parameter ratio of 7.5. The solvent system was modified (CH_2Cl_2 was added to EtOAc/hexane) in the hope of getting bigger crystals for better quality data. To our surprise, the structure solution and refinement proceeded routinely this time but in space group *Pbca* ($Z = 16$).[10] Yet another polymorph of **1**, form **D**, had been discovered.

Table 1. The conformation of 19 symmetry-independent molecules in tetramorphs of **1** (forms **A**–**D**).

Polymorph (space group)	Torsion angle[a] τ_1 [°]	τ_8 [°]	Crystallographic molecular designation	Intermolecular hydrogen bond synthon	Graph set notation
A ($P2_1$)	12.6(7)	12.5(8)	A_i	C–H···O	$C(8)$
B ($P\bar{1}$)	11.5(3)	17.7(3)	B_i	**II**	$R_2^2(20)$
	12.3(3)	16.0(3)	B_{ii}	**I**	$R_2^2(8)$
	14.9(3)	23.6(3)	B_{iii}	**I**	$R_2^2(8)$
	19.1(3)	31.8(3)	B_{iv}	**II**	$R_2^2(20)$
C ($P\bar{1}$)	20.1	31.5	C_i	**II**	$R_2^2(20)$
	20.9	30.8	C_{ii}	**II**	$R_2^2(20)$
	18.4	32.3	C_{iii}	**II**	$R_2^2(20)$
	12.1	22.7	C_{iv}	**I**	$R_2^2(8)$
	15.2	22.0	C_v	**I**	$R_2^2(8)$
	18.3	28.2	C_{vi}	**I**	$R_2^2(8)$
	12.8	16.0	C_{vii}	**I**	$R_2^2(8)$
	14.0	16.7	C_{viii}	**II**	$R_2^2(20)$
	10.2	21.0	C_{ix}	**II**	$R_2^2(20)$
	14.9	15.1	C_x	**I**	$R_2^2(8)$
	11.9	16.7	C_{xi}	**I**	$R_2^2(8)$
	11.5	17.4	C_{xii}	**II**	$R_2^2(20)$
D (*Pbca*)	18.5(2)	36.8(2)	D_i	C–H···O	$C(10)$
	8.4(2)	16.5(2)	D_{ii}	**III**	$R_2^2(16)$

[a] The estimated standard deviation (esd) of the torsion angle is given in parentheses. The esd values are not provided for form **C** because the *R* factor is high (0.11). A difference of more than 3° in the torsion angle ($\geq 3 \times$ esd) may be taken as representing different conformations.

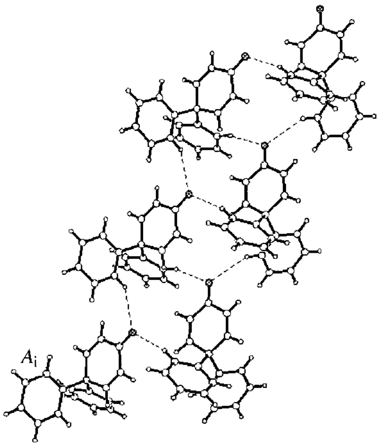
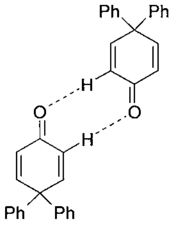


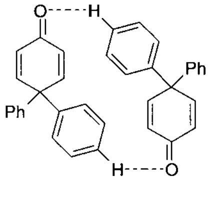
Figure 1. Helices of C–H···O hydrogen bonds ($C(8)$ graph set) between 2_1-related molecules in form **A** (conformer A_i).

We have thus characterized 19 crystallographically independent molecules of **1** in four crystal structures (**A**–**D**) that may be classified as conformational polymorphs.[11] Furthermore, forms **A**, **B**, and **C** are concomitant polymorphs because they crystallize from the same flask, and forms **B**, **C**, and **D** are conformational isomorphs because they have multiple conformations of **1** within the same crystal. There are only three examples known of systems with four polymorphs: pyrazinamide, sulfathiazole, and sulfapyridine.[12] A trimorphic system[13] with seven conformations of the molecule and a hexamorphic system[14] of conformational polymorphs with one symmetry-independent molecule in each crystal structure have been reported.

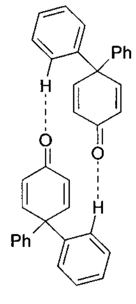
Form **A** consists of linear chains of C–H···O hydrogen bonds (d(H···O), $\sphericalangle$(C–H···O): 2.52 Å, 163.9°; 2.61 Å, 129.9°; neutron-normalized geometry) such that each molecule of **1** (A_i, Table 1) is bonded to four screw axis related molecules through phenyl hydrogen donors (Figure 1). There are four symmetry-independent molecules in crystal **B**. Molecules B_{ii} and B_{iii} engage in centrosymmetric C–H···O dimers with the quinone carbonyl group of different molecules (synthon **I**, 2.33 Å, 169.2°; 2.49 Å, 123.4°). Similarly molecules B_i and B_{iv} have distinct occurrences of centrosymmetric (Ph)C–H···O synthon **II** through the *para* hydrogen donor (2.64 Å, 137.9°; 2.75 Å, 121.5°; Figure 2). Each symmetry-independent molecule of form **B** (B_i–B_{iv}) is a different conformer of the title compound (Table 1). Polymorph **C** has 12 molecules in the asymmetric unit (C_i, C_{ii}, ..., C_{xii}). The structure has a complex and intricate crystal packing (not shown) mediated by multiple occurrences of C–H···O hydrogen bonded synthons **I** and **II** (Table 1). In the orthorhombic form **D**, D_i molecules are connected by C–H···O hydrogen bonds (2.36 Å, 138.0°; 2.55 Å, 166.9°; Figure 3a) and D_{ii} molecules are connected as centrosymmetric dimers through synthon **III** (2.57 Å, 144.6°); such dimers are in turn connected by C–H···O bonds



I
$R_2^2(8)$



II
$R_2^2(20)$



III
$R_2^2(16)$

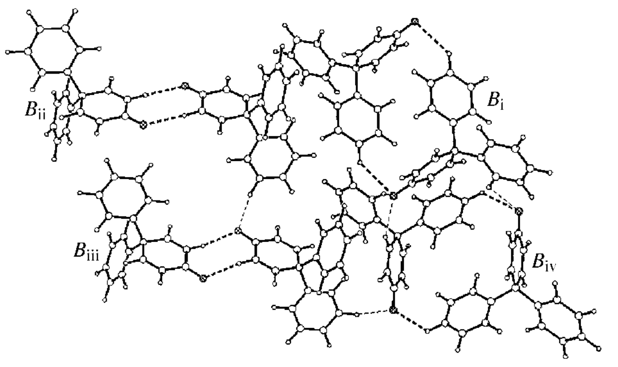


Figure 2. Centrosymmetric C–H···O synthons **I** (B_{ii}, B_{iii}; $R^2_2(8)$ motif) and **II** (B_i, B_{iv}; $R^2_2(20)$ motif) in form **B** shown as bold dotted lines. The C–H···O interactions are shown as normal dotted lines.

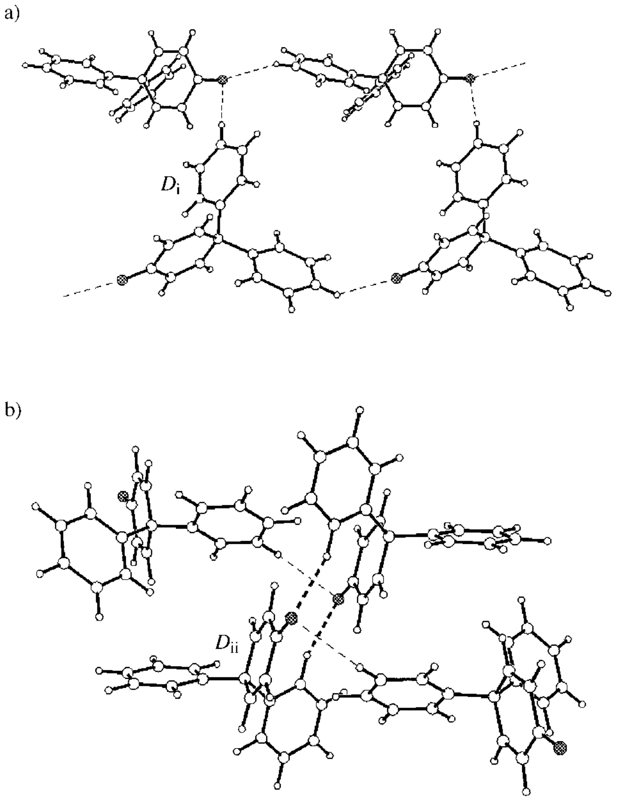


Figure 3. a) C–H···O hydrogen bonds between D_i molecules in form **D**. These molecules are related by a translation (left–right, $C(10)$ chain) and a screw axis (bottom–top). b) Centrosymmetric C–H···O synthon **III** between D_{ii} molecules (bold dotted lines, $R^2_2(16)$ motif) and C–H···O interactions (normal dotted lines).

(2.76 Å, 145.2°; Figure 3b). From the viewpoint of conformational polymorphism and conformational isomorphism, D_i and D_{ii} adopt new conformations (Table 1). To summarize, the tetramorphic crystal structures of **1** are stabilized by different arrangements of C–H···O hydrogen bonds.[15] The supramolecular synthon[16] description and graph set notation[17] of these motifs are given in Table 1.

The 19 crystallographically independent molecules of **1** differ in rotation about the C–C bond between the quinone and the phenyl ring. These different conformations may be classified through eight possible torsion angles (τ_1, τ_2, …, τ_8). We have selected τ_1 and τ_8, taken from a single asymmetric unit of the eight-dimensional torsion angle space, as the torsion parameters to map the conformational surface in these 19 molecules (Figure 4a). Similar scatter plots are obtained if other appropriate pairs of torsion angles are used. There are two populations of conformers (Figure 4b): $\tau_1 = 8.0–16.0°$, $\tau_8 = 12.0–24.0°$ and $\tau_1 = 18.0–22.0°$, $\tau_8 = 27.0–38.0°$. The motion of the phenyl rings in these conformations is correlated, that is, a change in the conformation of one phenyl ring leads to a conformational change in the second ring. Such a gearing of geminal phenyl rings has been noted earlier.[18] Notwithstanding that conformational change about a C–C single bond is a flexible (soft) parameter and that small differences in torsion parameters (2–3°) may not be chemically meaningful, it is clear that in our case there are two populations of conformers with mean values of $\tau_1 = 12°$, $\tau_8 = 18°$ and $\tau_1 = 20°$, $\tau_8 = 32°$.

A particular conformation is associated with a specific hydrogen bond synthon even if the molecules are present in different polymorphs. For example, B_i and C_{xii} molecules have nearly identical conformations and they engage in synthon **II** ($R^2_2(20)$ motif) in their respective crystal structures. Similarly, other conformations in forms **B** and **C** that are part of the same cluster in the τ_1–τ_8 scatter plot engage in synthons **I** and **II**. All this suggests that each of these conformations plays a specific structural role in the crystallization of these polymorphs. The two triclinic crystals present snapshot pictures at different stages of crystallization, from an evolving array of

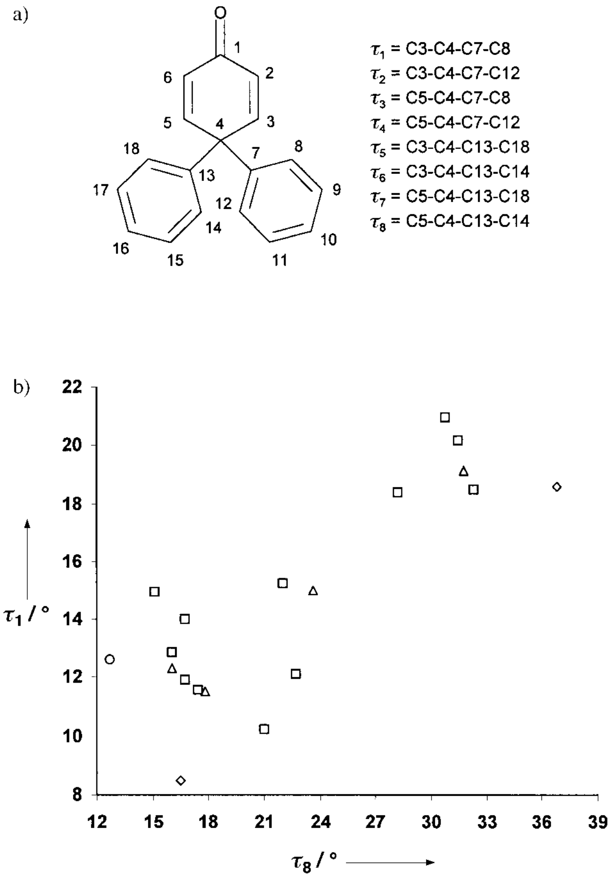


Figure 4. a) Definition of the torsion angles τ_1–τ_8 in **1**. b) The scatter plot of τ_1 versus τ_8. Note the two clusters of conformations and the near linear correlation. Absolute values of torsion angles are used. Symbols for the polymorphs: **A** = ○, **B** = △, **C** = □, **D** = ◇.

ordered molecules in many conformations (form **C**, $Z' = 12$) to a more compact lattice (form **B**, $Z' = 4$). Their similarity may be judged from the calculated powder X-ray diffraction trace (Cerius^2,[19] see the Supporting Information). A frequently posed question about conformational polymorphs is the following:[20] Does molecular conformation determine crystal packing or vice versa? We show herein that the flexible conformations of **1** result in different crystal packing arrangements through the hydrogen bond synthons and graph set patterns listed in Table 1. The chemical basis for the simultaneous occurrence of conformational polymorphism and concomitant polymorphism is that the energy scale of these two events are comparable (1–2 kcal mol^{-1}). The difference between the two extreme values of Z' ($\Delta Z' = 11$) in tetramorphs of **1** is the highest known to date.[21] Despite the presence of different Laue symmetries, there is no compromise in crystal compactness because the density of these forms is about the same (1.23–1.25 g cm^{-3}).

To conclude, polymorphism in compound **1** is significant for several reasons. This is the first example of four polymorphs with 19 crystallographically independent conformations of the same molecule to be characterized by low-temperature X-ray diffraction. Such systems may serve as an accurate benchmark for the refinement of atom–atom potentials in crystal structure prediction programs.[22] In addition to being an example of conformational polymorphism, **1** also exhibits conformational isomorphism (forms **B**, **C**, and **D**) and concomitant polymorphism (forms **A**, **B**, and **C**). Further studies on temperature- or pressure-mediated phase transition, kinetic and thermodynamic measurements, and molecular and lattice energies as well as the search for new polymorphs[23] and characterization of their morphology are the focus of continuing experiments with **1**.

Experimental Section

Compound **1**[24] was crystallized from EtOAc/*n*-hexane (5/95) at ambient temperature. Three types of morphologies were observed: needle, block, and plate. The needle-shaped crystals correspond to the **A** polymorph as verified by the space group determination of ca. 10 different crystals. Forms **B** and **C** crystallize concomitantly with **A** from the same flask. Crystals of form **D** were obtained by adding CH_2Cl_2 to the above solvent system. The experimental powder X-ray diffraction trace of the bulk material matches with the simulated trace of the monoclinic form **A**[10] (see the Supporting Information).

Received: March 25, 2002
Revised: June 4, 2002 [Z18964]

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[8] Polymorphism of **1** in terms of type and number of forms is based on the crystallographic analysis of stable structures. Extensive examples of polymorphism may be found in the thermomicroscopy literature (M. Kuhnert-Brand stätter, *Thermomicroscopy in the Analysis of Pharmaceuticals*, Pergamon, Oxford, **1971**) and in Groth's collection (P. H. R. Groth, *Chemische Kristallographie, Vol. 1–5*, Engelmann, Leipzig, **1906–1919**). However, some of these are transient phases observed during heating or cooling without crystallographic confirmation.

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[10] Crystal data: Polymorph **A**:[9] CSD refcode HEYHUO (CCDC-1294/26). Polymorph **B**:[9] CSD refcode HEYHUO01 (CCDC-1294/25). Polymorph **C**: triclinic, space group $P\bar{1}$, $a = 18.3788(4)$, $b = 19.9701(4)$, $c = 24.4423(5)$ Å, $\alpha = 95.008(1)°$, $\beta = 111.688(1)°$, $\gamma = 105.218(1)°$, $V = 7871.8(3)$ Å^3, $Z = 24$, $\rho_{calcd} = 1.247$ g cm^{-3}, $T = 140(2)$ K, $R1 = 0.1121$, $wR2 = 0.1885$ for all data, 16805 independent reflections. Polymorph **D**: orthorhombic, space group *Pbca*, $a = 10.7921(6)$, $b = 17.4749(12)$, $c = 27.9344(19)$ Å, $V = 5268.2(6)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.242$ g cm^{-3}, $T = 100(2)$ K, $R1 = 0.0589$, $wR2 = 0.1360$ for all data, 6538 independent reflections. CCDC-182230 and -182231 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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[23] A fifth unstable polymorph was grown from a solution of **1** in EtOH/CH_2Cl_2 during the course of writing this manuscript. Approximate cell dimensions: $a = 8.39$, $b = 14.56$, $c = 26.80$ Å, $\alpha = 90.36°$, $\beta = 90.02°$, $\gamma = 90.03°$. It changes to form **B** with time.

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