Dilemmas in Crystallization. The 'Unusual' Behavior of *trans*-1,5-Dichloro-9,10-diethynyl-9,10-dihydroanthracene-9,10-diol and the More 'Normal' Behavior of Its Pseudopolymorphs with Dipolar Aprotic Solvents

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Dedicated to Professor *Jack D. Dunitz* on the occasion of his 80th birthday

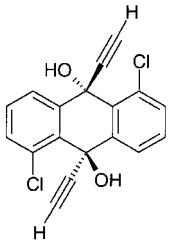
The compound *trans*-1,5-dichloro-9,10-diethynyl-9,10-dihydroanthracene-9,10-diol (DDDA) has an inversion center as the only molecular symmetry element and yet does not occupy an inversion center in the centrosymmetric space group that it adopts in the crystal structure. The reason for this very unusual occurrence is the crowded environment of the H-bond donors and acceptors that leads to less than optimal H-bonding. A centrosymmetric supramolecular synthon constituted with four Cl-atoms in a planar array occupies an ***i*** site in the crystal, and this appears to provide a satisfactory alternative packing. Based on the hypothesis that H-bonding is less than optimal in the crystal structure of DDDA, pseudopolymorphs were prepared with strongly H-bond-accepting solvents. The crystal structures of five of these solvates are described, wherein the DDDA molecule is able to occupy an ***i*** site and form strong and linear O–H ··· O H-bonds with the solvent molecules. Competition experiments show that a smaller solvent molecule with a greater H-bond-accepting ability is included more readily and that the H-bonds formed are correspondingly better.

1. Introduction. – The theory of close packing forms the basic framework of our understanding of the ways in which organic molecules assemble into crystals. To the extent that isotropic forces are important in the early stages of crystallization, the resulting crystal structures will more nearly approximate to the closest packed ones. However, all non-hydrocarbons contain atoms that can give rise to anisotropic forces, and, therefore, to interactions that have preferred directionality. The resulting crystal structures deviate from closest packing in some way or the other [1]. The challenge of crystal engineering is that, while these deviations are not marked, there is still sufficient variability and subtlety in the crystal structures that are obtained, so as to make their prediction a difficult matter [2]. During crystallization of organic molecules, directionality of approach may be achieved without significant loss in packing efficiency [3]. In this respect, the grammar of crystal packing of organic [4] and inorganic [5] compounds is different.

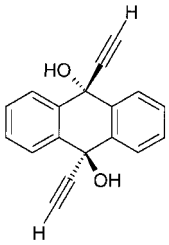
Kitaigorodskii [6], and independently *Nowacki* [7], outlined several consequences of the close-packing principle as applied to organic molecular solids. In general, it was shown that only *ca.* 20 of the possible 230 space groups are actually utilized. In the context of the present work, three consequences are pertinent: *1*) centrosymmetric space groups are preferred; *2*) space groups that contain translational symmetry elements like screw axes and glide planes are preferred; *3*) the inversion center is the

only molecular symmetry element that is routinely carried over into the crystal structure. In other words, molecules that have the symmetry element ***i*** usually occupy a $\bar{1}$ site in the crystal.

This work was prompted by the observation that the title molecule, *trans*-1,5-dichloro-9,10-diethynyl-9,10-dihydroanthracene-9,10-diol (DDDA), which has a molecular inversion center, does not occupy this site symmetry in the crystal. Although the space group is centrosymmetric ($P2_1/n$), the molecule lies on a general position in the unit cell. This occurrence was deemed to be sufficiently uncommon, and a more-detailed study was undertaken.



DDDA



DDA

2. Results and Discussion. – 2.1 *Molecular and Crystal Symmetry.* DDDA is one among a much larger group of geminal alkynols that is being examined in our laboratories to investigate H-bond patterns in compounds wherein the donor and acceptor groups are sterically hindered [8]. The close juxtaposition of two H-bond donors and two acceptors in the geminal alkynols and also the possibility of their incorporation into cooperative networks means that the four (in principle) possible interactions O–H ··· O, C–H ··· O, O–H ··· π, and C–H ··· π become competitive. The unusually high levels of interaction interference that are, therefore, possible may generate different and unpredictable H-bond networks [9]. The title molecule DDDA was prepared from 1,5-dichloro-9,10-anthraquinone and recrystallized from EtOH/benzene 1:1. The crystal structure was determined. *Table 1* gives the crystallographic data. *Fig. 1* shows a single molecule of DDDA, and *Fig. 2* shows the perspective packing diagram. Both show very clearly that the molecule does not lie on a crystallographic inversion center. While we were accustomed to unpredictable crystal structures in this family of compounds [8], the present result was felt to be exceptional even by these standards.

But exactly how uncommon is such an occurrence? It has been shown recently that it is possible to answer such a question computationally [10]. An algorithm that perceives molecular symmetry has been applied to *ca.* 200000 entries from the *Cambridge Structural Database* (*CSD*) [11]. For each molecule, the perceived point group, together with crystallographic properties such as the space group, occupied *Wyckoff* positions, and the number of residues in the asymmetric unit have been placed in a relational database, CSDSymmetry. Queries may be posed to this database to obtain information on relationships between molecular and crystal symmetry. It was found, *e.g.*, that 18008 molecules belong to point groups containing the symmetry element ***i***. Of these, 17152 molecules (95.2%) crystallize in space groups containing a

Table 1. *Crystallographic Data and Structure Refinement Parameters.*

	DDDA	DDDA · $(DMSO)_2$	DDDA · DMSO	DDDA · $(NMP)_2$	DDDA · $(HMPA)_2$	DDDA · $(DMF)_2$
Solvent[a])	EtOH/benzene 1 : 1	DMSO	DMSO/DMF 1 : 1	NMP	HMPA	DMF
Empirical formula	$C_{18}H_{10}Cl_2O_2$	$(C_{18}H_{10}Cl_2O_2)$ $\cdot (C_2H_6OS)_2$	$C_{18}H_{10}Cl_2O_2$ $\cdot C_2H_6OS$	$C_{18}H_{10}Cl_2O_2$ $\cdot (C_5H_9NO)_2$	$C_{18}H_{10}Cl_2O_2$ $\cdot (C_6H_{18}N_3OP)_2$	$C_{18}H_{10}Cl_2O_2$ $\cdot (C_3H_7NO)_2$
	329.16	485.42	407.29	527.42	687.57	475.35
Crystal system	monoclinic	triclinic	triclinic	triclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2_1$
a [Å]	7.4205(2)	6.6307(5)	7.3174(15)	7.4173(15)	8.5057(2)	7.3834(3)
b [Å]	12.7571(4)	7.6581(5)	9.3646(19)	9.1696(18)	9.7689(2)	15.3739(8)
c [Å]	14.8695(4)	11.9717(7)	14.222(3)	9.6472(19)	10.7323(2)	10.3430(5)
α [°]	90	79.613(2)	81.14(3)	103.40(3)	86.9450(10)	90
β [°]	93.3820(10)	84.232(2)	89.16(3)	90.46(3)	77.4350(10)	102.497(2)
γ [°]	90	67.037(2)	67.56(3)	102.70(3)	84.8540(10)	90
Z'	1	0.5	1	0.5	0.5	1
Volume [Å^3]	1405.16(7)	550.26(6)	889.0(3)	621.5(2)	866.37(3)	1146.23(9)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
D_{calc} [g/cm^3]	1.556	1.465	1.522	1.409	1.318	1.377
μ [mm^{-1}]	0.465	0.512	0.501	0.300	0.323	0.317
2θ [°]	4.20 – 57.98	3.90 – 54.98	4.76 – 54.98	4.34 – 54.98	3.90 – 54.98	4.04 – 54.96
Range h	– 10 to 9	– 8 to 8	– 9 to 9	– 9 to 9	– 11 to 11	– 9 to 9
Range k	– 17 to 17	– 9 to 9	– 12 to 11	– 11 to 11	– 12 to 12	– 19 to 19
Range l	– 20 to 20	– 15 to 15	– 18 to 18	– 12 to 12	– 13 to 13	– 13 to 13
Reflns. collected	16581	6206	10782	7131	9911	11510
Unique reflns.	3207	2530	4079	2848	3965	4895
Observed reflns.	2702	2385	3749	2701	3727	4233
R_1 ($/I > 2\,\sigma(I)$)	0.0328	0.0388	0.0325	0.0322	0.0325	0.0576
wR_2 (all)	0.0853	0.0948	0.0895	0.0871	0.0886	0.1539
Goodness-of-fit	1.031	1.061	1.059	1.031	1.041	1.182
T [K]	120(2)	120(2)	120(2)	120(2)	120(2)	120(2)
CCDC deposition number	200403	200399	200400	200401	200402	200398
Crystal size	0.40 × 0.18 × 0.08	0.36 × 0.32 × 0.1	0.48 × 0.35 × 0.18	0.44 × 0.32 x 0.30	0.42 × 0.32 × 0.16	0.38 × 0.35 × 0.20

[a]) NMP = 1-methylpyrrolidin-2-one; HMPA = hexamethylphosphoric triamide.

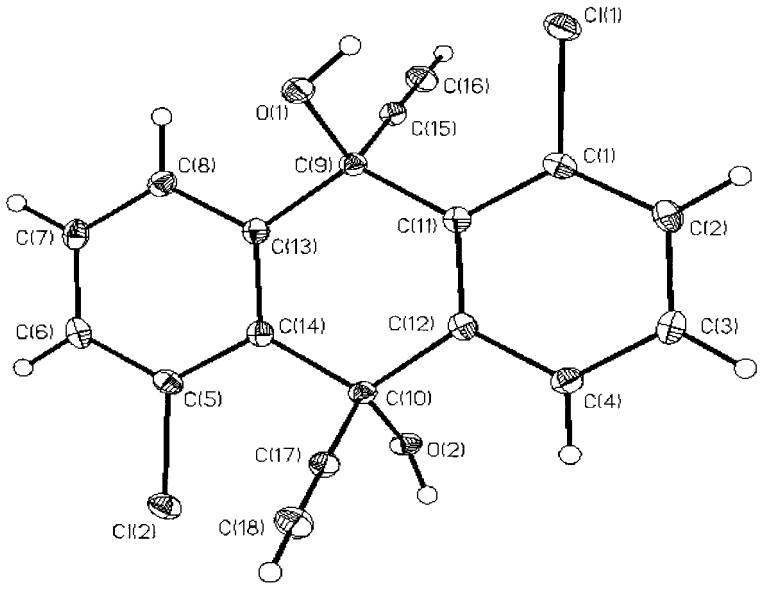


Fig. 1. *Single-molecule ORTEP drawing of DDDA*

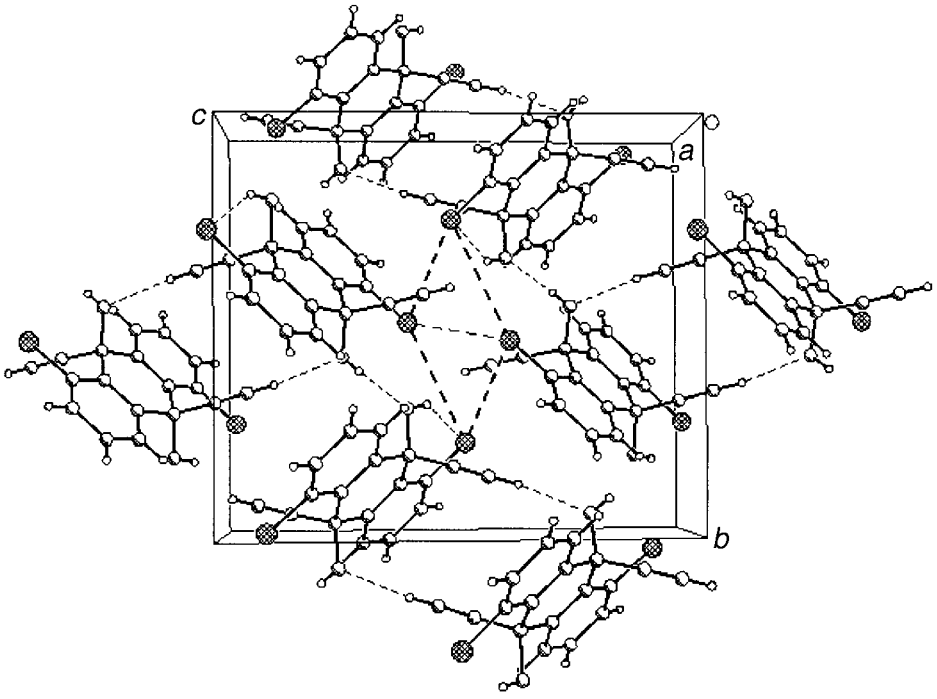


Fig. 2. *Packing diagram of DDDA*. Notice the planar Cl_4 synthon (highlighted) at the position (0.5, 0.5, 0.5). C–H···O H-bridges are also shown.

Wyckoff position of symmetry ***i***, and of these, 15156 molecules (88.4%) lie on a crystallographic inversion center. If additionally it is stipulated that the molecule contains ***i*** as the *only* molecular symmetry element (DDDA is in this category), 99% of such molecules lie on an inversion center in the crystal [12]. These numbers are compelling. So, while the behavior of the title molecule is not unprecedented, it is certainly unusual. *Kitaigorodskii*'s generalizations are not laws, but there should be good reasons why exceptions exist.

No other symmetric geminal alkynol among the nearly 135 present in the *CSD* and/or studied by us displays such behavior. An important molecule for comparison is the non-chloro-analogue *trans*-9,10-diethynyl-9,10-dihydroanthracene-9,10-diol (DDA), which lies on an inversion center in space group $P\bar{1}$ [8]. With respect to changes in crystal structure brought about by changes in molecular structure, the following may be noted: *1*) substituent groups in a molecule exert both geometric and chemical effects that lead to the crystal packing adopted; *2*) the effects of substitution depend not only on the nature of the substituent but also on its positioning in the molecule; *3*) changes may be carried out over a range of substituent groups without perturbing the crystal structure but, at the limit of the range, a small change in the molecular structure may cause a large change in the crystal packing. In the context of DDDA and DDA, the introduction of the two Cl substituents at a position proximal to the already crowded alkynol functionality has resulted in such a change.

Any observed crystal structure is a free-energy minimum [6], and, if a particular feature that favors close-packing, such as a centrosymmetrical molecule lying on a crystal inversion center is absent, then it may be presumed that there are other compensating factors in the packing that reduce the free energy. Hence the H-bonds and other intermolecular interactions in the crystal structure of DDDA were closely examined, and *Fig. 2* shows two main patterns of interactions. There is a cooperative arrangement of three H-bonds, an intermolecular C–H ⋯ O from the ethynyl group ($d = 2.44$ Å, $\theta = 164.7°$), an intermolecular O–H ⋯ O between OH groups ($d = 1.83$ Å, $\theta = 173.8°$), and a weak intramolecular O–H ⋯ Cl ($d = 2.25$ Å, $\theta = 135.4°$). The difference in local environment of the two OH groups in the molecule is apparent. One forms an intermolecular O–H ⋯ O bond, while the other forms an intramolecular O–H ⋯ Cl bond. The second pattern, which is more distinctive, is the supramolecular synthon consisting of four Cl-atoms. This four-atom synthon is built up with four quasi type-II Cl ⋯ Cl contacts (3.56, 3.69 Å) and one type-I Cl ⋯ Cl contact (3.64 Å) [13][1]). A third synthon may be derived from the first in that it is a C–H ⋯ O dimer formed between two inversion-related interactions.

The four-atom 'Cl_4' synthon lies on the inversion center in the crystal and is the dominant feature in the packing. It has been noted that crystal symmetry may be analyzed as a convolution of molecular symmetry and supramolecular synthon (or void) symmetry [14]. The underlying reason why centrosymmetric molecules tend to lie on inversion centers in the crystal is that the largest number of atoms are then able to aggregate with the shortest possible separations. This is nearly true if a densely packed

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[1]) In confirmation of the geometrical role of the Cl-atom in various compounds, generally we note that type-I Cl ⋯ Cl interactions are manifestations of pure close packing and that they do not arise from polarization. In contrast, the Cl ⋯ Cl contacts of type-II are polarization-induced and direction-dependent.

and symmetrical supramolecular synthon (like the planar Cl_4) were to lie on an inversion center. Such a supramolecular synthon may be likened to a molecule turned 'inside out' and has a similar function in crystal packing, as does a molecule. The equivalence of these two situations is demonstrated by the fact that the tetrahedral molecule CBr_4 and the tetrahedral synthon 'Br_4' play exactly the same role in crystal packing, so much so that the crystal structures of the pair of compounds $[C(C_6H_5)_4 : CBr_4]$ and $[C(C_6H_4Br)_4]$ are nearly identical [15]. In short, supramolecular synthons may be considered as being equivalent to molecules insofar as their roles as modules for close packing – provided they are sufficiently compact. It may be no coincidence that the C–H ··· O dimer synthons occupy the other set of inversion centers in the structure. To summarize, this is a structure where all the special positions are occupied by voids with little detriment to close-packing (C_k 0.716).

Even if the observed packing is not particularly unfavorable, why does DDDA adopt this unusual variant? In most of the geminal alkynol structures, the dominant mode of association is a cooperative chain of O–H ··· O H-bonds and/or loops of weak and strong H-bonds to give elaborate networks [8]. We suggest that the already crowded environment in the region of the OH and ethynyl groups is made even more hindered by the presence of the Cl substituents in DDDA, so that extensive H-bond networks are not possible. For instance, only one of the two OH groups participates in O–H ··· O H-bonding; the second is relegated to a somewhat feeble intramolecular O–H ··· Cl interaction. Again, only one of the two ethynyl groups forms a H-bond; the other is completely 'free'. To mitigate this situation, the Cl substituents assemble into the centrosymmetric Cl_4 synthon with the above-reported consequences. To corroborate this suggestion, we searched the *CSD* (ConQuest 1.4, Version 5.23, April 2002) for this four-atom cluster. Of the 2918 hits with an aromatic Cl substituent, there are 298 cases of the Cl_4 tetramer. This is a respectable number and shows that this synthon can very well be structure-determining.

2.2. *Pseudopolymorphism.* It was felt that an 'unusual' and, therefore, 'disagreeable' packing was obtained for DDDA because of the difficulty in forming an adequate number of short and linear H-bonds. Noting also that a molecule with unsatisfied H-bonding potential tends to form solvated crystals from solvents with a complementary H-bonding propensity [16][17], we decided to crystallize DDDA from several dipolar aprotic solvents (DMSO, *N*-methylpyrrolidin-2-one (NMP), hexamethylphosphoric triamide (HMPA), DMF) in the search for pseudopolymorphs. We were successful beyond our most-optimistic expectations. Five solvates were obtained and characterized by X-ray diffraction. These are DDDA · DMSO, DDDA · $(DMSO)_2$, DDDA · $(NMP)_2$, DDDA · $(HMPA)_2$, and DDDA · $(DMF)_2$. These crystal structures are now described.

Table 2 provides a comparison of the five solvates with regard to selected solvent and crystal properties. *Fig. 3* shows the crystal structures. All the solvates provide an excellent demonstration of directed inclusion of small molecular guests. In all five crystal structures, there are good O–H ··· O H-bonds formed by the OH groups of DDDA and the O-atom acceptor of the solvent. These are the most important intermolecular interactions in the structures, justifying the hypothesis that the H-bonding in the unsolvated crystal is somehow insufficient or unsatisfactory. In contrast to the unsolvated DDDA wherein only one of the OH groups is engaged in O–H ··· O

H-bonding, both these groups are so bonded in the solvates. The packing efficiencies are generally high, but as mentioned in the introduction, the packing coefficient is an insensitive indicator of actualities in organic molecular crystals.

DDDA · (DMSO)$_2$: The DDDA molecule lies on an inversion center and donates strong O–H ··· O bonds ($d = 1.71$ Å, $\theta = 172.4°$) to the S=O groups of two guest molecules (*Fig. 3,a*). This constitutes the centrosymmetric solute/solvent 1:2 module. These modules are linked along [100] by short and linear C–H ··· O bonds ($d = 2.14$ Å; $\theta = 163.9°$) to complete the structure in which the host and guest domains are segregated. The C–H ··· O bond is from the acidic ethynyl group to the OH group of DDDA and is cooperative with the O–H ··· O bond. Clearly of importance is the small size and good H-bonding ability of DMSO. The small size of the solvent molecule allows it to make a linear approach in the O–H ··· O H-bond.

DDDA · DMSO: This is a variation of the 1:2 solvate in which an 'extra' molecule of DDDA interleaves between the 1:2 modules *via* O–H ··· O bonds ($d = 1.76$ Å, $\theta = 169.5°$; $d = 1.96$ Å, $\theta = 149.8°$) to give a host-rich structure (*Fig. 3,b*). The ethynyl groups become 'free' as a consequence, but there is a C–H ··· O bond ($d = 2.45$ Å, $\theta = 159.1°$) between the activated Me group of DMSO and an OH group of DDDA.

DDDA · (NMP)$_2$: The solute/solvent 1:2 module is again found on an inversion center (O–H ··· O; $d = 1.75$ Å, $\theta = 172.4°$), and these modules are connected to each other *via* C–H ··· Cl bonds ($d = 2.67$ Å, $\theta = 172.4°$). As in DDDA · (DMSO)$_2$, the host and guest domains are distinct (*Fig. 3,c*).

DDDA · (HMPA)$_2$: In this structure too, the solute/solvent 1:2 module is found (O–H ··· O; $d = 1.70$ Å, $\theta = 165.9°$; $d = 1.71$ Å, $\theta = 161.4°$). As in other HMPA solvates, there is a plethora of weak C–H ··· O interactions (*Fig. 3,d*). The structure is triclinic and centrosymmetric, and from a packing viewpoint, it is hardly distinguishable from the 1:2 solvates with DMSO and NMP.

DDDA · (DMF)$_2$: The structure is pseudocentrosymmetric, and the 1:2 module is a recurring theme (O–H ··· O; $d = 1.70$ Å, $\theta = 176.2°$; $d = 1.72$ Å, $\theta = 173.8°$). As in DDDA · (DMSO)$_2$, the modules are linked with C–H ··· O bonds ($d = 2.19$ Å, $\theta = 159.3°$; $d = 2.30$ Å, $\theta = 154.3°$) to form a criss-cross arrangement in which solute and solvent domains are integrated (*Fig. 3,e*).

These five crystal structures show that the presence of a dipolar aprotic solvent allows for better H-bonding by DDDA. In every case, a solute/solvent 1:2 module is seen, mediated by O–H ··· O H-bonds, the module lies on an inversion center (or a pseudoinversion center), and any packing deficiencies that might be present in the unsolvated DDDA are seemingly avoided. To complete the study, we carried out competition experiments in which DDDA was crystallized from solvent mixtures. The mixtures selected were DMSO/DMF, DMSO/HMPA, HMPA/DMF, NMP/HMPA, and NMP/DMF. In each experiment, several crystals were selected (>6) and examined on the diffractometer. In every case, we obtained only a single pseudopolymorph. These were the 1:2 solvates with, respectively, DMSO, DMSO, HMPA, NMP, and NMP. Accordingly, we conclude that the preference for solvent inclusion in this system is in the following order: DMSO > NMP > HMPA > DMF. This order may be rationalized on the basis of the size of the solvent molecule and its H-bond-acceptor ability (*Table 2*). Generally, a smaller solvent molecule with a greater acceptor ability is included more easily, and the H-bonds formed are correspondingly better. These

Table 2. *Comparison of the Five Solvates with Regard to Selected Solvent and Crystal Properties*

Solvent	Host/guest ratio	Space group	Packing coefficient	Solvent surface area [Å^2/u.c.]	Solvent volume [Å^3/u.c.]	Acceptor strength		H-Bridges			
						electrostatic	*Mulliken*	interaction	*d* [Å]	*D* [Å]	*θ*
DMSO	1:1 (*Fig. 3,b)*	$P\bar{1}$	73.0	101.04	72.05	– 0.521	– 0.784	C–H···O	2.32	3.258(2)	142.9
								C–H···O	2.45	3.491(2)	159.1
								O–H···O	1.76	2.733(2)	169.5
								O–H···O	1.96	2.853(2)	149.8
DMSO	1:2 (*Fig. 3,a)*	$P\bar{1}$	70.6	101.04	72.05	– 0.521	– 0.784	C–H···O	2.14	3.184(2)	163.9
								C–H···O	2.42	3.538(2)	167.2
								O–H···O	1.71	2.682(2)	172.4
NMP	1:2 (*Fig. 3,c)*	$P\bar{1}$	70.2	134.45	102.72	– 0.622	– 0.620	C–H···O	2.41	3.277(2)	135.3
								C–H···O	2.45	3.443(2)	150.9
								C–H···Cl	2.67	3.752(1)	172.4
								O–H···O	1.74	2.726(2)	172.4
HMPA	1:2 (*Fig. 3,d)*	$P\bar{1}$	68.7	221.53	179.35	– 0.702	– 0.579	C–H···O	2.27	3.274(5)	153.2
								C–H···O	2.36	3.343(5)	149.9
								O–H···O	1.70	2.667(4)	165.9
								O–H···O	1.71	2.667(4)	161.4
								C–H···Cl	2.62	3.706(6)	176.1
DMF	1:2 (*Fig. 3,e*)	$P2_1$(pseudo $P2_1/n$)	72.5	108.40	78.65	– 0.553	– 0.579	C–H···O	2.19	3.227(5)	159.3
								C–H···O	2.30	3.312(5)	154.3
								O–H···O	1.70	2.689(5)	176.1
								O–H···O	1.71	2.695(4)	173.8

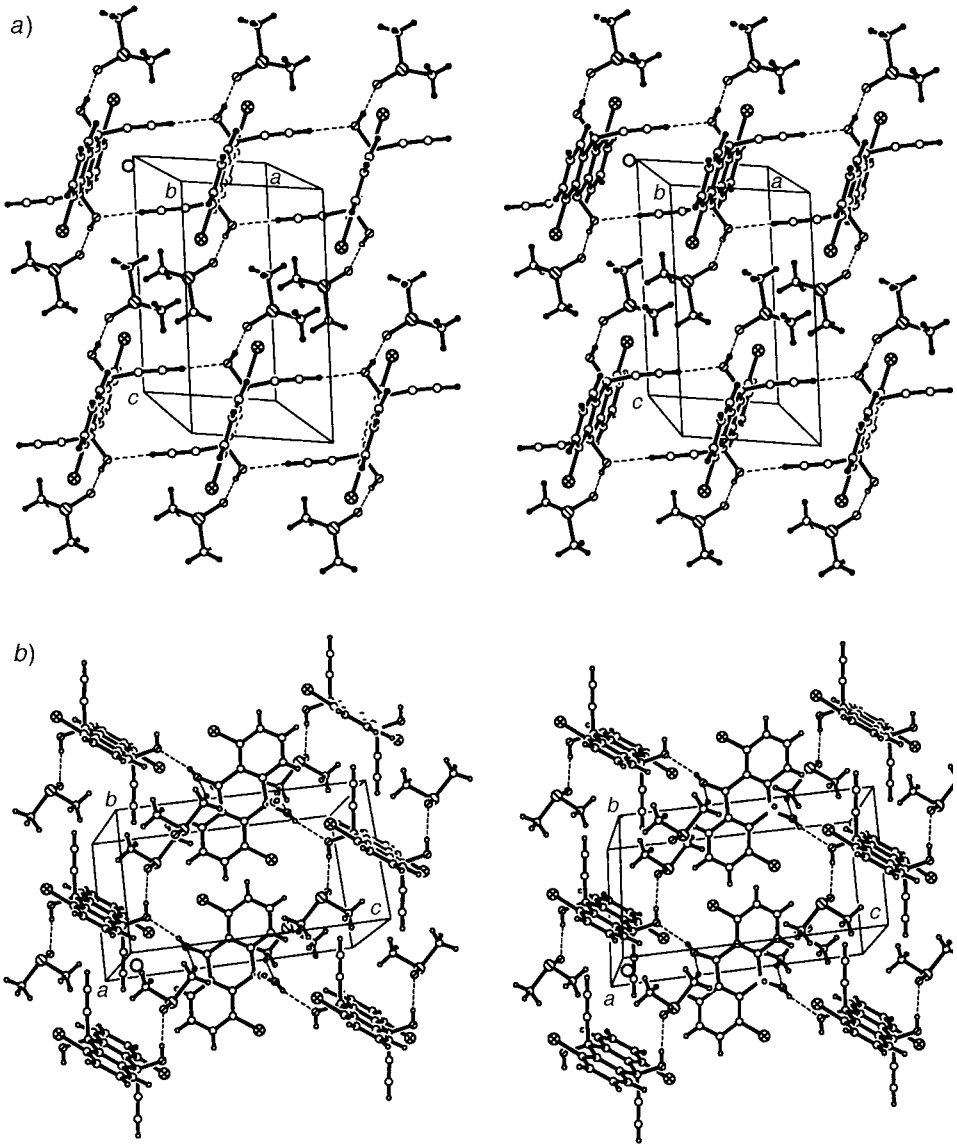

Fig. 3. *Stereoviews of a*) *DDDA · (DMSO)*$_2$. (notice the O–H···O and C–H···O interactions), *b*) *DDDA · DMSO*, *c*) *DDDA · (NMP)*$_2$ (the C–H···O dimer synthon is again observed); *d*) *DDDA · (HMPA)*$_2$, (notice the C–H···Cl dimer synthon), *and e*) *DDDA · (DMF)*$_2$

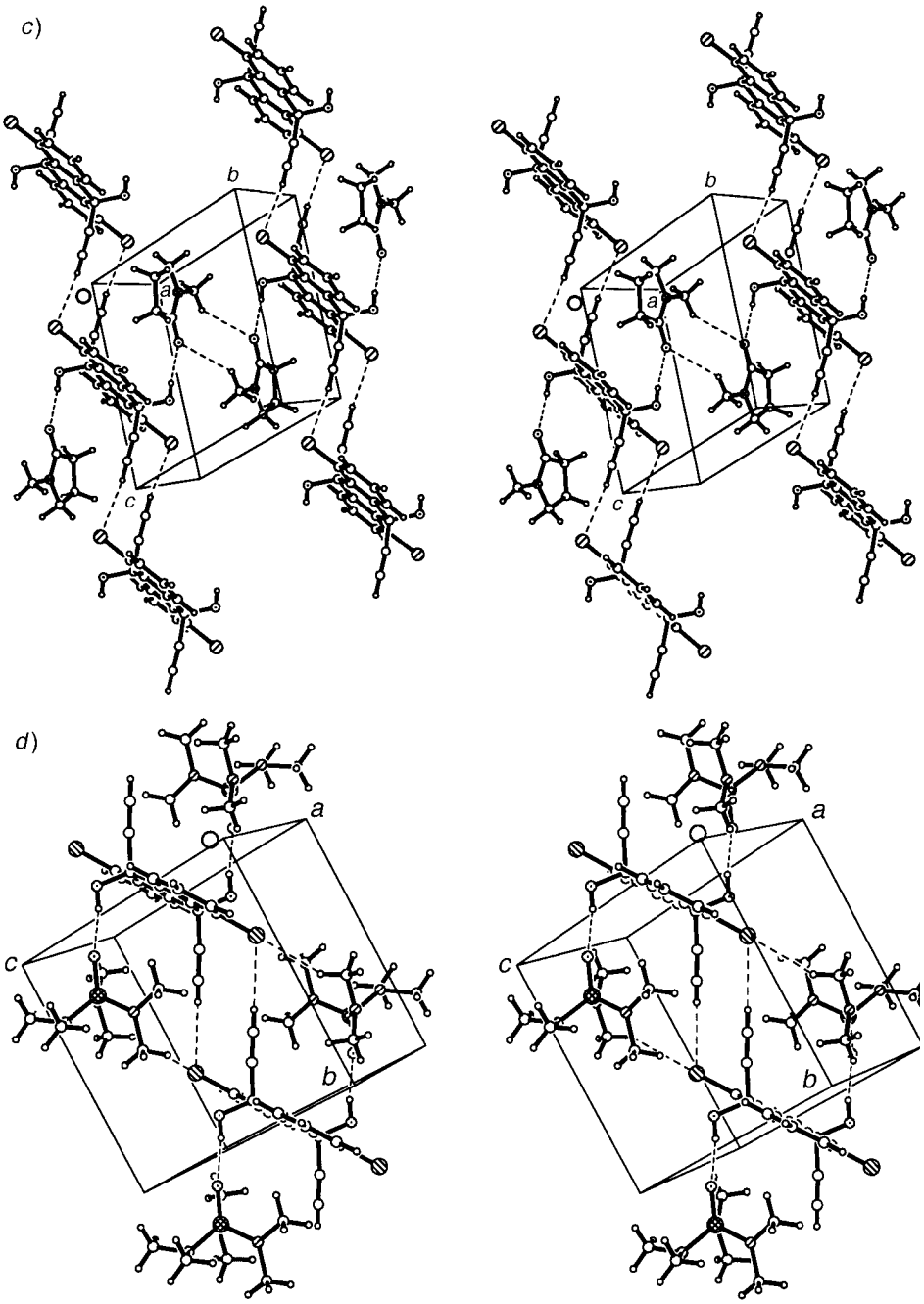

Fig. 3 (cont.)

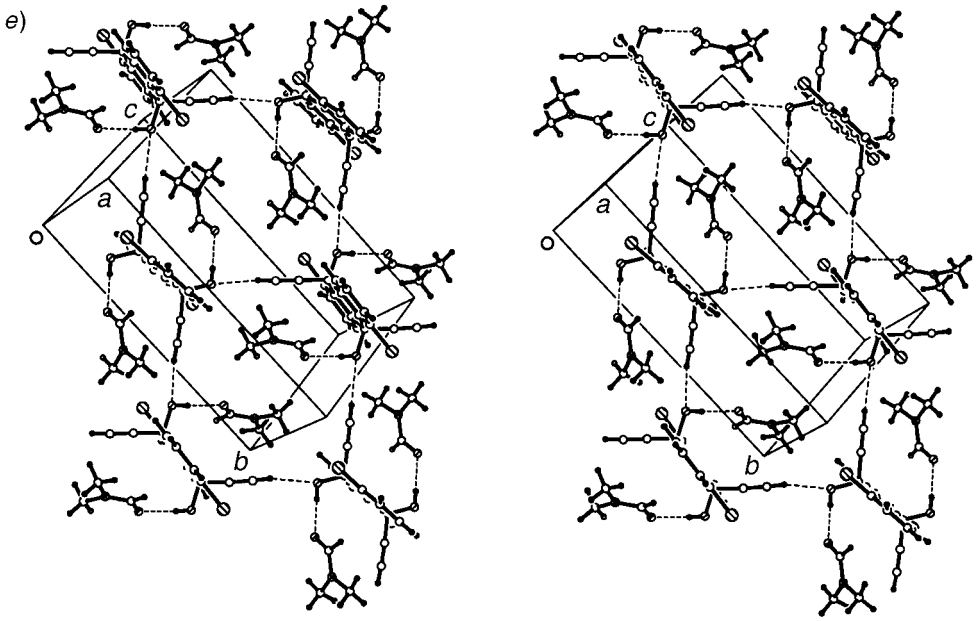

Fig. 3 (cont.)

observations are in accord with the fact that both chemical and geometric factors are important in crystal-structure stabilization.

3. Conclusions. – We have described the crystal structure of a C_i-symmetric molecule DDDA and have noted a seemingly 'unusual' occurrence, namely its presence on a general position in a centrosymmetric space group. This has been ascribed to unsatisfactory H-bonding brought about by steric hindrance of the H-bond donor and acceptor groups in the molecule. Solvates of DDDA in which it can form good O–H ··· O H-bonds to the solvent avoid this problem, and the DDDA molecule can now lie on an inversion (or pseudoinversion) center to give a more or less 'normal' structure.

However, designations such as 'normal' and 'unusual' are necessarily subjective. All crystal structures seek out free-energy minima, as pointed out by *Kitaigorodskii* [6], and in the end, no crystal structure is either 'normal' or 'unusual'. Perhaps better epithets would be 'understandable' and 'incomprehensible'. What is clear is that for a molecule like DDDA, crystallization to give a one-component crystal is fraught with dilemma. The unsolvated crystal contains an uncommon symmetry feature, but, then, solvation itself is not that common either. According to a recent analysis, solvation may be termed 'interrupted crystallization' [9]. In the most typical of crystallizations, in other words, when a single-component ordered crystal is obtained, solvent is expelled from a solute-solvent cluster into the bulk at the time of nucleation because of the entropic advantage in so doing. Solvation implies that this entropic gain is more than offset by the enthalpic gain in retaining the solvent in the crystal. This is especially true when the solvent is able to form strong and directional interactions like H-bonding with

the solute. In other words, when there are difficulties in forming the solvent-free crystal, solvation by an appropriate solvent remains a respectable way out, or shall we term it a dead end?

We conclude with the realization that, as the subject of crystal engineering evolves to include a larger number of 'exotic' compounds specially made for the experiments being contemplated, there will also be a greater number of 'unusual' occurrences that must gradually become more 'normal' as our understanding of crystal packing and ultimately of crystallization itself progresses.

Experimental Part

General. Solvents were purified by standard methods and dried if necessary. Reagents used were of commercial quality. DDDA was characterized by NMR and IR spectra, and corresponding pseudopolymorphs were characterized by their NMR Spectra. M.p.: *Fisher-Jones* melting-point instrument. IR spectra: *Jasco 5300* spectrometer; in cm^{-1}. ^{1}H-NMR Spectra: at 200 MHz, *Bruker ACF* instrument; δ in ppm, J in Hz.

Synthesis. DDDA was synthesized from, 1,5-dichloro-9,10-anthraquinone by a two-step procedure. All operations were carried out under dry N_2 by means of standard syringe-septum technique. A soln. of (trimethylsilyl)acetylene (4.4 mmol) in THF (15 ml) was mixed with BuLi (4.2 mmol) at 195K. After stirring for 15 min, a soln. of 1,5-dichloro-9,10-anthraquinone was added dropwise, and stirring was continued for 30 min at 195K and for a further hour at r.t. Brine was added to the mixture, and the products were extracted with Et_2O. The org. phase was dried ($MgSO_4$) and evaporated. The residue was dissolved in MeOH, and KOH/MeOH was added slowly and the mixture stirred for 1h at r.t. H_2O was added, the mixture extracted with AcOEt, the extract dried ($MgSO_4$) and evaporated, and the residue purified by column chromatography (30% AcOEt/hexane) followed by recrystallization: 60% of trans-*1,5-dichloro-9,10-diethynyl-9,10-dihydroanthracene-9,10-diol* (DDDA). Crystals. M.p. 533K (dec.) ^{1}H-NMR (200 MHz $CDCl_3$): 8.10 (*dd*, $J = 8, 3$, 2 H *peri*); 7.51 (*m*, 4 H), 4.46 (s, 2 H); 2.70 (s, 2 H). IR: 3312, 3288, 3177, 3001, 2881, 2116, 1973, 1811, 1595, 1562, 1456, 1300, 1205, 1039, 679, 515.

Crystallization. Crystals of DDDA were grown from EtOH/benzene 1:1 at r.t. Diffraction-quality crystals of all pseudopolymorphs of DDDA were prepared by crystallizing DDDA from the respective solvents. The presence of solvent in these pseudopolymorphs were confirmed by ^{1}H-NMR.

Crystal-Structure Analysis. X-Ray-diffraction intensities for DDDA and its pseudopolymorphs were collected at 120K (*Oxford-Cryosystems* cryostat) on a *Bruker SMART-CCD* diffractometer (*Bruker Systems Inc.*) using Mo$K\alpha$ X-radiation. Data were processed by using the *Bruker SAINT* package (*Bruker Systems Inc.*) with structure solution and refinement using SHELX97 [18]. The structures of all the compounds were solved by direct methods and refined by full-matrix least-squares on F^2. H-Atoms were located in all six structures and refined freely with isotropic displacement parameters. Crystal data and details of data collections, structure solutions, and refinements are summarized in *Table 1*. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-200398 to 200403 (see *Table 1*). Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ UK (fax: + 44 (1223) 336 033; e-mail: deposit@ccdc.cam.ac.uk)

Calculations. All calculations were carried out on *Indigo Solid-Impact* and *Indy* workstations from *Silicon Graphics.* All interatomic distances and related calculations were carried out with the PLATON programme [19]. The computations of acceptor strength of all solvent molecules were calculated with the *Hartree-Fock ab initio* method at the 6-31G* level. The solvent volumes were at the AM1 level calculated using the Cerius ^{2} program [20].

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