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References

Cesario, M., Guilhem, J. & Martin, J.-C. (1977). Fourth European Crystallographic Meeting, Oxford, England, pp. 458–460.

Chiang, J. F. & Bauer, S. H. (1969). *J. Am. Chem. Soc.* **91**, 1898–1901.

Grynkiewicz, G., Priebe, W. & Zamojski, A. (1979). *Carbohydr. Res.* **68**, 33–41.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

Kojić-Prodić, B., Rogić, V. & Ruzić-Toroš, Z. (1976). *Acta Cryst.* B**32**, 1833–1838.

Krajewski, J. W., Urbańczyk-Lipkowska, Z. & Gluziński, P. (1978). *Acta Cryst.* A**34**, S86.

Krajewski, J. W., Urbańczyk-Lipkowska, Z. & Gluziński, P. (1979). *Acta Cryst.* B**35**, 519–522.

Krajewski, J. W., Urbańczyk-Lipkowska, Z., Gluziński, P., Bleidelis, J. & Kemme, A. (1978). *Acta Cryst.* A**34**, S85–S86.

Krajewski, J. W., Urbańczyk-Lipkowska, Z., Gluziński, P., Bleidelis, J. & Kemme, A. (1979). *Acta Cryst.* B**35**, 1248–1250.

López de Lerma, J., Martínez-Carrera, S. & García-Blanco, S. (1973). *Acta Cryst.* B**29**, 537–541.

Roberts, P. & Sheldrick, G. M. (1975). Program *XANADU*. Univ. of Cambridge, England.

Schwartz, J. C. P. (1973). *J. Chem. Soc. Chem. Commun.* pp. 505–508.

Sheldrick, G. M. (1976). *SHELX* 76. Program for crystal structure determination. Univ. of Cambridge, England.

Stewart, J. M., Kundell, F. A. & Baldwin, J. C. (1970). The XRAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Stokhuyzen, R. & Chung Chieh (1976). *J. Chem. Soc. Perkin Trans.* 2, pp. 481–483.

Vangehr, K., Luger, P. & Paulsen, H. (1979). *Carbohydr. Res.* **70**, 1–11.

Acta Cryst. (1979). B**35**, 2629–2634

The Crystal and Molecular Structure of 1,5-Diphenylcarbazone

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Abstract

Crystals of 1,5-diphenylcarbazone, $C_{13}H_{12}N_4O$, are triclinic, space group $P\bar{1}$, $a = 9{\cdot}639\,(1)$, $b = 11{\cdot}250\,(1)$, $c = 12{\cdot}840\,(1)$ Å, $\alpha = 74{\cdot}82\,(1)$, $\beta = 86{\cdot}33\,(1)$, $\gamma = 67{\cdot}37\,(1)°$, $V = 1239$ Å^3, $Z = 4$. The structure was determined from three-dimensional diffractometer data by the multi-solution technique (*MULTAN*) from 2010 independent reflections and refined by a least-squares block-diagonal approximation to a final R value of 0·075. The asymmetric unit contains two molecules of different conformation having nearly identical bond distances and bond angles. The diphenylcarbazone molecule differs from its sulphur analogue, dithizone. It is not planar and there is only π-electron delocalization in the hydrazo chain of the molecule. The molecules in the cell are held together by N—H···O hydrogen bonds while two other N—H···O hydrogen bonds join the molecules of successive cells in chains parallel to [100].

Introduction

1,5-Diphenylcarbazone (hereinafter DPCO) forms highly coloured metal complexes that provide the basis for its use as a sensitive reagent for the detection and colorimetric determination of metal ions. In particular, those reactions with Cr^{VI}, Cr^{III} and Cr^{II} have been studied in this laboratory (Willems, Blaton, Peeters & De Ranter, 1977).

The IR spectrum of pure DPCO in $CHCl_3$ or CCl_4 shows two absorption bands in the 3000–4000 cm^{-1} region at 3410 and 3350 cm^{-1}. As the DPCO concentration increases the intensity of the two bands decreases and three new bands appear at 3275, 3195 and 3075 cm^{-1}. Kemula & Janowski (1966) ascribe: (i) the 3410 cm^{-1} band to free N—H stretching vibration of

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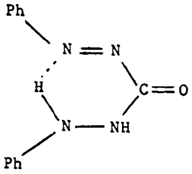
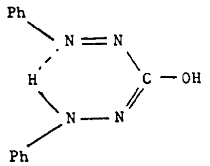
the N—H group in the β position to the C=O group; (ii) the 3350 cm^{-1} band to free N—H stretching vibration of the N—H group in the α position; (iii) the new bands at 3275, 3195 and 3075 cm^{-1} to intermolecular bonded N—H stretching vibrations. Willems & Zeegers-Huyskens (1976) assign the 3410 cm^{-1} band to free $\nu_{\text{N-H}}$ vibration and the 3350 cm^{-1} band to intramolecular bonded $\nu_{\text{N-H}}$ vibration (form I).

From IR measurements on DPCO powder (KBr pellets) we conclude that in the solid DPCO is present only as the keto form: the ν_{OH} stretching band is absent and the $\nu_{\text{C=O}}$ stretching band is strong (1707 cm^{-1}). In the 3000–4000 cm^{-1} region four absorption bands are present. The 3375 cm^{-1} band is attributed to the intramolecular bonded $\nu_{\text{N-H}}$ vibration and the bands at 3275, 3195 and 3075 cm^{-1} to intermolecular bonded $\nu_{\text{N-H}}$ vibration (Kemula & Janowski, 1966; Willems & Zeegers-Huyskens, 1976).

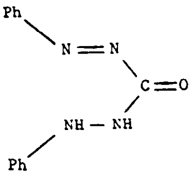
The visible spectrum in apolar solvents shows two absorption maxima: one at about 455 nm and another with much lower intensity at 565 nm. Kemula & Janowski (1966) ascribe the 565 nm band to the pseudo six-ring form (I) of DPCO, while Willems & Zeegers-Huyskens (1976) attribute this band to the enol form (II) present in low concentration. The 455 nm absorption band is generally attributed to the 'free' keto form (III).



(I)



(II)



(III)

From the above considerations it has to be concluded that the golden yellow colour of the DPCO crystals is associated with the keto form (III).

In order to elucidate the molecular configuration and the character of the hydrogen bonds a determination of the structure was undertaken.

Experimental

As has been shown (Willems & De Ranter, 1974), none of the DPCO reagents available commercially are pure, but they can be purified by column chromatography on polyamide powder. After purification, very fine laths (with morphological needle axis *a*) were obtained by slow evaporation from a methanol–carbon tetrachloride solution.

Crystal data

$C_{13}H_{12}N_4O$, $M_r = 240{\cdot}27$, triclinic (no mirror symmetry was found in the oscillation and Weissenberg photographs). Unit-cell parameters (determined from rotation and Weissenberg photographs and refined by least-squares refinement of the 2θ angles for 25 reflections, Cu $K\alpha$ radiation, $\lambda = 1{\cdot}54178$ Å): $a = 9{\cdot}639$ (1), $b = 11{\cdot}250$ (1), $c = 12{\cdot}840$ (1) Å, $\alpha = 74{\cdot}82$ (1), $\beta = 86{\cdot}33$ (1), $\gamma = 67{\cdot}37$ (1)°, $V = 1239$ Å^3, $Z = 4$, $D_m = 1{\cdot}292$, $D_c = 1{\cdot}287$ Mg m^{-3}, $F(000) = 504$. Space group $P\bar{1}$. $\mu(\text{Cu } K\alpha) = 0{\cdot}714$ mm^{-1}.

A crystal of $0{\cdot}05 \times 0{\cdot}1 \times 0{\cdot}3$ mm was used for data collection on an automated Nonius CAD-4 single-crystal diffractometer with graphite monochromator. By means of the θ–2θ scan technique a total of 1817 independent reflections with $I \geq 3\sigma(I)$ were obtained within $\sin\theta/\lambda < 0{\cdot}4587$ Å^{-1}. One standard reflection scanned after every fortieth measurement suffered no significant loss of intensity during data collection. Corrections for Lorentz and polarization factors were made in the usual way but no correction was made for absorption.

Determination and refinement of the structure

The structure was solved, not without difficulty, with the *MULTAN* procedures (Main, Woolfson, Lessinger, Germain & Declercq, 1974). With the program running in its routine way 32 phase sets were created, several of them with a high combined figure of merit. None of them, however, yielded a Fourier map corresponding to a valuable solution. Different starting reflections were selected from the bottom of the *CONVERGE* map, care being taken to ensure good interlinking properties with the higher-order reflections [origin-defining: 311 ($|E| = 3{\cdot}80$), $2\bar{1}\bar{1}$ ($|E| = 2{\cdot}76$), 481 ($|E| = 2{\cdot}43$); starting-set: $20\bar{1}$ ($|E| = 4{\cdot}54$), 221 ($|E| = 2{\cdot}49$), $1\bar{6}4$ ($|E| = 2{\cdot}06$), $1\bar{3}\bar{5}$ ($|E| = 1{\cdot}75$), $46\bar{2}$ ($|E| = 1{\cdot}73$)]. The E_{min} value was set to 1·60. The E map calculated with the set of phases with the highest combined figure of merit revealed two DPCO molecules in the asymmetric unit together with some spurious peaks. The R value at this point was 0·29. Structure factor calculations followed by Fourier refinement gradually reduced the R value to 0·16. Further refinement was performed by full-matrix least-squares analysis using the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with $w = \sigma(F_{\text{rel}})^{-2}$. The atomic scattering factors for the non-hydrogen atoms were taken from Cromer & Mann (1968) and those for H from Stewart, Davidson & Simpson (1965). The refinement of the overall scale factor and all atomic positional and isotropic thermal parameters converged at an R of 0·14. Block-diagonal least-squares refinement in which the anisotropic temperature parameters were varied reduced R to 0·12.

A difference-Fourier synthesis yielded the positions of the 24 H atoms (electron density range 0·3–0·5 e

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	Molecule *A*				Molecule *B*			
	x	y	z	$B_{eq.}$ or B (Å^2)	x	y	z	$B_{eq.}$ or B (Å^2)
O(1)	1522 (4)	5779 (3)	804 (3)	5·5 (1)	−3685 (4)	6508 (4)	172 (3)	4·9 (1)
N(1)	2737 (5)	7280 (4)	−84 (4)	4·1 (2)	−1695 (5)	5483 (5)	1508 (4)	5·2 (2)
N(2)	1519 (5)	8067 (5)	−509 (4)	4·4 (2)	−2242 (5)	4660 (5)	1892 (4)	5·1 (2)
N(3)	3980 (5)	5346 (4)	1154 (3)	3·9 (1)	−1434 (5)	6750 (4)	−135 (4)	4·5 (2)
N(4)	4283 (5)	4069 (4)	1802 (3)	4·0 (1)	−1797 (6)	7403 (5)	−1222 (3)	5·0 (2)
C(1)	2624 (6)	6071 (5)	666 (4)	3·8 (2)	−2393 (6)	6292 (5)	454 (4)	3·9 (2)
C(2)	1607 (6)	9264 (5)	−1222 (4)	3·9 (2)	−1559 (6)	3771 (6)	2932 (4)	4·2 (2)
C(3)	2947 (6)	9352 (6)	−1620 (5)	4·9 (2)	−2069 (8)	2743 (6)	3298 (5)	5·8 (2)
C(4)	2901 (7)	10560 (7)	−2260 (5)	5·6 (2)	−1502 (9)	1842 (7)	4277 (5)	6·5 (3)
C(5)	1583 (8)	11634 (6)	−2508 (5)	5·9 (2)	−491 (8)	1990 (8)	4886 (5)	6·6 (3)
C(6)	267 (7)	11532 (6)	−2121 (5)	5·3 (2)	0 (8)	3029 (9)	4506 (6)	7·4 (3)
C(7)	251 (7)	10333 (6)	−1488 (5)	4·9 (2)	−521 (7)	3936 (7)	3503 (5)	5·8 (2)
C(8)	3987 (6)	3911 (6)	2909 (4)	4·0 (2)	−2462 (6)	8796 (5)	−1521 (4)	3·8 (2)
C(9)	4124 (7)	2655 (6)	3507 (5)	5·3 (2)	−3147 (6)	9520 (5)	−791 (4)	4·3 (2)
C(10)	3963 (8)	2409 (7)	4611 (5)	6·8 (2)	−3855 (6)	10889 (6)	−1149 (5)	5·1 (2)
C(11)	3653 (9)	3430 (9)	5112 (5)	7·3 (3)	−3887 (7)	11533 (6)	−2218 (5)	6·0 (2)
C(12)	3493 (8)	4683 (7)	4519 (5)	6·6 (2)	−3217 (8)	10818 (7)	−2942 (5)	6·4 (2)
C(13)	3654 (7)	4930 (6)	3418 (5)	5·3 (2)	−2487 (7)	9439 (6)	−2622 (5)	5·4 (2)
H(3)	4067	8402	−1327	4·9	−2739	2591	2716	5·8
H(4)	3891	10468	−2651	5·2	−1838	1054	4667	6·4
H(5)	1567	12574	−3123	5·7	−177	1266	5800	6·6
H(6)	−649	12368	−2238	5·7	950	2875	4940	7·0
H(7)	−802	10096	−1115	5·8	−27	4781	3108	5·3
H(9)	4506	2073	3029	5·0	−3025	9038	−1	3·8
H(10)	3773	1482	5066	6·5	−4437	11437	−584	4·5
H(11)	3669	3152	5928	6·6	−4517	12554	−2394	5·2
H(12)	3554	5558	4878	6·5	−3018	11253	−3826	5·5
H(13)	3373	5921	2975	5·0	−1919	8823	−3112	4·6
H(N3)	4850	5591	1057	4·1	−344	6682	−67	4·8
H(N4)	3981	3554	1347	4·0	−1509	6994	−1794	5·2

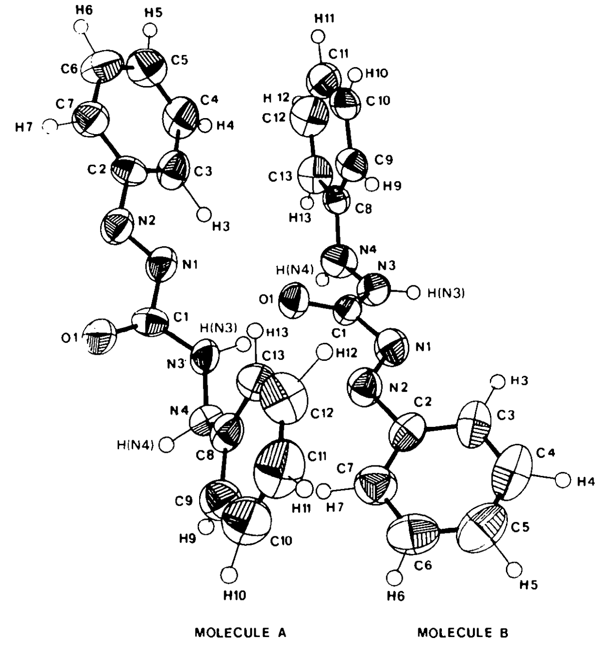


Fig. 1. A perspective drawing of the molecules in the asymmetric unit. Non-hydrogen atoms are represented by thermal ellipsoids at the 50% probability level, whereas the H atoms have arbitrary 0·1 Å radius spheres. The atomic numbering scheme is shown.

Table 2. *Selected torsion angles* (°)

	Molecule *A*	Molecule *B*
O(1)–C(1)–N(1)–N(2)	6·6 (11)	27·0 (10)
O(1)–C(1)–N(3)–N(4)	7·5 (12)	−9·7 (12)
C(1)–N(1)–N(2)–C(2)	178·6 (6)	177·2 (6)
C(1)–N(3)–N(4)–C(8)	−89·4 (10)	96·5 (10)
N(1)–N(2)–C(2)–C(3)	16·8 (11)	8·1 (10)
N(3)–N(4)–C(8)–C(9)	172·3 (6)	164·7 (7)

Å^{-3}). They were included as a fixed-atom contribution with constant isotropic thermal parameters equal to those of the carrier atoms. In the final cycles of refinement, weights were used according to Cruickshank's (1965) formula: $w = (30{\cdot}0 + F_o + 0{\cdot}0128F_o^2)^{-1}$. The R value was 0·075 for all observed reflections. The average and the maximum shift:error ratios for the non-hydrogen atoms were respectively 0·34 and 1·3. In a final difference-Fourier synthesis the highest electron density did not exceed 0·41 e Å^{-3}. No other significant features were noted in this map. All the calculations were performed on the KU Leuven IBM 370/158 computer. Atomic coordinates are given in Table 1. A perspective view of the asymmetric unit, which contains

Table 3. *Bond lengths* (Å) *and angles* (°)

	Molecule *A*	Molecule *B*
O(1)–C(1)	1·218 (9)	1·233 (9)
C(1)–N(1)	1·484 (13)	1·453 (14)
N(1)–N(2)	1·220 (12)	1·217 (11)
N(2)–C(2)	1·446 (13)	1·457 (15)
C(1)–N(3)	1·334 (12)	1·329 (11)
N(3)–N(4)	1·387 (13)	1·393 (12)
N(4)–C(8)	1·409 (8)	1·399 (11)
C(2)–C(3)	1·388 (11)	1·371 (13)
C(3)–C(4)	1·377 (14)	1·397 (16)
C(4)–C(5)	1·358 (14)	1·389 (16)
C(5)–C(6)	1·368 (12)	1·370 (15)
C(6)–C(7)	1·386 (14)	1·378 (16)
C(7)–C(2)	1·380 (13)	1·386 (13)
C(8)–C(9)	1·380 (13)	1·406 (12)
C(9)–C(10)	1·382 (11)	1·391 (13)
C(10)–C(11)	1·386 (14)	1·357 (14)
C(11)–C(12)	1·369 (15)	1·371 (13)
C(12)–C(13)	1·378 (11)	1·381 (12)
C(13)–C(8)	1·388 (13)	1·373 (13)
N(3)–H(N3)	0·971	1·031
N(4)–H(N4)	1·044	0·939
C(3)–H(3)	1·185	1·106
C(4)–H(4)	1·031	1·054
C(5)–H(5)	1·138	1·220
C(5)–H(6)	0·996	1·036
C(7)–H(7)	1·188	1·205
C(9)–H(9)	0·969	1·007
C(10)–H(10)	1·130	1·066
C(11)–H(11)	1·010	1·042
C(12)–H(12)	1·213	1·148
C(13)–H(13)	1·046	1·034
O(1)–C(1)–N(1)	127·0 (4)	124·0 (6)
O(1)–C(1)–N(3)	126·2 (5)	126·3 (5)
N(1)–C(1)–N(3)	106·7 (5)	109·7 (5)
C(1)–N(1)–N(2)	111·9 (5)	110·8 (6)
N(1)–N(2)–C(2)	112·5 (5)	114·3 (6)
N(2)–C(2)–C(3)	123·3 (5)	123·5 (6)
N(2)–C(2)–C(7)	115·2 (6)	113·6 (6)
C(3)–C(2)–C(7)	121·5 (6)	122·9 (6)
C(2)–C(3)–C(4)	118·2 (5)	117·1 (8)
C(3)–C(4)–C(5)	121·2 (7)	120·8 (9)
C(4)–C(5)–C(6)	120·2 (6)	120·1 (7)
C(5)–C(6)–C(7)	120·8 (5)	120·3 (8)
C(6)–C(7)–C(2)	118·0 (6)	118·6 (8)
C(1)–N(3)–N(4)	120·1 (6)	119·3 (5)
N(3)–N(4)–C(8)	118·4 (5)	118·8 (5)
N(4)–C(8)–C(9)	117·1 (6)	117·4 (6)
N(4)–C(8)–C(13)	123·0 (6)	122·2 (5)
C(9)–C(8)–C(13)	119·7 (6)	120·4 (5)
C(8)–C(9)–C(10)	120·0 (7)	118·1 (6)
C(9)–C(10)–C(11)	119·8 (7)	121·4 (6)
C(10)–C(11)–C(12)	120·4 (7)	119·6 (6)
C(11)–C(12)–C(13)	120·0 (8)	121·2 (7)
C(12)–C(13)–C(8)	120·2 (7)	119·3 (6)
C(1)–N(3)–H(N3)	126·1 (5)	138·6 (5)
N(4)–N(3)–H(N3)	113·6 (4)	101·7 (5)
N(3)–N(4)–H(N4)	106·9 (4)	124·9 (5)
C(8)–N(4)–H(N4)	121·4 (5)	115·7 (5)
C(2)–C(3)–H(3)	117·3 (6)	120·1 (5)
C(4)–C(3)–H(3)	124·3 (6)	122·6 (8)
C(3)–C(4)–H(4)	111·8 (5)	125·9 (9)
C(5)–C(4)–H(4)	125·4 (6)	111·2 (7)
C(4)–C(5)–H(5)	119·1 (7)	122·2 (8)
C(6)–C(5)–H(5)	120·3 (5)	117·3 (8)
C(5)–C(6)–H(6)	117·6 (6)	113·3 (6)
C(7)–C(6)–H(6)	121·2 (7)	126·2 (9)
C(6)–C(7)–H(7)	113·9 (5)	123·4 (8)
C(2)–C(7)–H(7)	128·0 (5)	116·9 (6)
C(8)–C(9)–H(9)	106·4 (6)	115·3 (6)
C(10)–C(9)–H(9)	132·6 (7)	126·5 (6)
C(9)–C(10)–H(10)	119·7 (8)	112·2 (6)
C(11)–C(10)–H(10)	118·5 (7)	125·6 (7)
C(10)–C(11)–H(11)	115·2 (8)	126·4 (6)
C(12)–C(11)–H(11)	124·1 (9)	113·7 (7)
C(11)–C(12)–H(12)	125·6 (7)	119·9 (5)
C(13)–C(12)–H(12)	112·3 (7)	118·8 (6)
C(12)–C(13)–H(13)	121·4 (6)	122·3 (7)
C(8)–C(13)–H(13)	117·9 (7)	118·1 (5)

two molecules of DPCO, is shown in Fig. 1. Dihedral angles describing the conformation of the two molecules are presented in Table 2.*

Discussion

The molecules are not planar and have different conformations. This is probably the result of the hydrogen-bonding network which determines the cohesion of the molecules and which will be discussed later. Inspection of the bond lengths and angles, given in Table 3, reveals that they are in no way exceptional, although some differences exist between the two molecules (maximum 0·03 Å in bond lengths and 2° in bond angles).

According to bond lengths and bond orders between C and N atoms in which both atoms are assumed to have sp^2 hybridization, the azo chain [C(1)–N(1)–N(2)–C(2)] has localized single [C(1)–N(1) 1·484 (13), 1·453 (14); N(2)–C(2) 1·446 (13), 1·457 (15) Å] and double [N(1)–N(2) 1·220 (12), 1·217 (11) Å] bonds. In the hydrazo chain [C(1)–N(3)–N(4)–C(8)] the N–N and C–N bonds are formally single and one expects two sp^3-hybridized N atoms. This does not really fit, however, with the experimental data.

The fact that in both molecules all angles around N(3) [C(1)–N(3)–N(4) 120·1 (6), 119·3 (5)°] and N(4) [N(3)–N(4)–C(8) 118·4 (5), 118·8 (5)°] are very close to 120° might create the impression that the N atoms are sp^2-hybridized. But then the short distances C(1)–N(3) [1·334 (12), 1·329 (11) Å] and C(8)–N(4) [1·409 (8), 1·399 (11) Å] disagree with the findings of Burke-Laing & Laing (1976) who, on the basis of accurately known crystal structures, deduced a value of 1·45 Å for a single C(sp^2)–N(sp^2) bond. Calculating the bond orders (Pauling, 1960) gives 1·2 for C(8)–N(4) and 1·5 for C(1)–N(3).

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34655 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

That the C(1)—N(3) bond has pronounced double-bond character is in agreement with the conclusions of Burke-Laing & Laing (1976). They point out that the π electrons on N in a C—N chain are delocalized if this atom is involved in three σ bonds, especially if a N—H group is present, because intermolecular hydrogen bonding facilitates delocalization, or if a C=O group is adjacent.

The shortening of the C(8)—N(4) bond is due to the interaction of the π-electron sextet of the benzene ring with the lone pair of N(4). This interaction is possible because the benzene ring is nearly parallel to the N(3)—N(4) bond [dihedral angle N(3)—N(4)—C(8)—C(9) 172·3 (6), 164·7 (7)°]. Delocalization between the atoms N(3) and N(4) is impossible in view of the dihedral angles C(1)—N(3)—N(4)—C(8) in both molecules [−89·4 (10), 96·5 (10)°].

The C—O bond lengths [1·218 (19), 1·233 (9) Å] have not changed compared with a normal double bond (1·23 Å) in a ketone (*International Tables for X-ray Crystallography*, 1968). The distances are comparable with those found in related compounds such as carbohydrazide [1·242 (2) Å] (Domiano, Pellinghelli & Tiripicchio, 1972), 1,5-diphenylcarbonohydrazide [1·235 (4) Å] (De Ranter, Blaton & Peeters, 1979) and diphenylcarbodiazone [1·235 (4) Å] (Blaton, Peeters, Willems & De Ranter, 1977). This indicates that from the two possible tautomeric (keto or enol) conformations, the keto form is present. An even stronger indication is the explicit location of the H[N3*A*(*B*)] and H[N4*A*(*B*)] atoms, whose positions could be detected from the electron density difference map. Although the remaining background density around the O atom does not exclude completely the presence of some small enol contribution, we feel that on the whole (the low electron density at the right distance from the O atom, IR and UV spectra) any enol contribution will be very small. Bond distances and angles in all phenyl groups are satisfactory: the mean C—C distance is 1·38 Å. Equations of the planes through the phenyl rings and the deviations of the atoms from the planes are given in Table 4.

The packing of the DPCO molecules in the crystal structure is determined by hydrogen bonds (Table 5) as shown in Fig. 2. The hydrogen-bond network can be depicted by taking the two DPCO molecules in the asymmetric unit as a pair joined by the hydrogen bond between N(3*A*) and O(1*B*) [3·066 (16) Å]. This pair is linked to the symmetry-related pair by hydrogen bonds between O(1*B*) and N(4A^{i}) and between O(1B^{i}) and N(4*A*) [2·920 (11) Å]. Each pair of DPCO molecules is in turn connected to its translation equivalents along the *a* axis by hydrogen bonds [N(3*B*)—O(1A^{ii}) 2·850 (17) Å] giving rise to two parallel chains. There are no other close contacts between the chains so that packing in the [010] and [001] directions is only due to van der Waals forces. The dihedral angles between the planes of the phenyl rings and the N—CO—N groups, listed in Table 4, show that the phenyl group of the hydrazo chain (planes 2 and 5) is almost perpendicular to the N—CO—N group (planes 3 and 6), while the

Table 4. *Least-squares planes and atom deviations* (Å)

The equations of the planes are expressed in direct space as $PX + QY + RZ = S$. The atoms listed are those included in the plane calculation. E.s.d.'s are in the range 0·011–0·015 Å.

Plane 1: $3\cdot00116X + 6\cdot48907Y + 11\cdot93202Z = 5\cdot02554$

C(2*A*)	0·007	C(4*A*)	−0·004	C(6*A*)	0·011
C(3*A*)	0·002	C(5*A*)	−0·002	C(7*A*)	−0·013

Plane 2: $9\cdot32508X + 1\cdot99891Y + 1\cdot83264Z = 5\cdot02252$

C(8*A*)	0·008	C(10*A*)	0·001	C(12*A*)	−0·006
C(9*A*)	−0·009	C(11*A*)	0·006	C(13*A*)	0·000

Plane 3: $-0\cdot33842X + 6\cdot96767Y + 11\cdot23559Z = 4\cdot88563$

O(1*A*)	−0·002	N(1*A*)	−0·001
C(1*A*)	0·006	N(3*A*)	−0·001

Plane 4: $-5\cdot08287X + 5\cdot20048Y + 7\cdot51707Z = 4\cdot95681$

C(2*B*)	0·002	C(4*B*)	0·004	C(6*B*)	−0·013
C(3*B*)	−0·008	C(5*B*)	0·006	C(7*B*)	0·008

Plane 5: $9\cdot42909X + 5\cdot71174Y + 3\cdot14200Z = 2\cdot22114$

C(8*B*)	0·000	C(10*B*)	−0·001	C(12*B*)	0·000
C(9*B*)	0·000	C(11*B*)	0·000	C(13*B*)	0·000

Plane 6: $-0\cdot04143X + 9\cdot68954Y + 7\cdot47456Z = 6\cdot44962$

O(1*B*)	0·001	N(1*B*)	0·001
C(1*B*)	−0·003	N(3*B*)	0·001

Acute angles (°) between planes (e.s.d.'s are in the range 0·7–1·2°)

1 and 2	71·9	4 and 5	69·8	1 and 5	60·2
1 and 3	23·3	4 and 6	33·3	2 and 4	53·2
2 and 3	85·6	5 and 6	79·5		

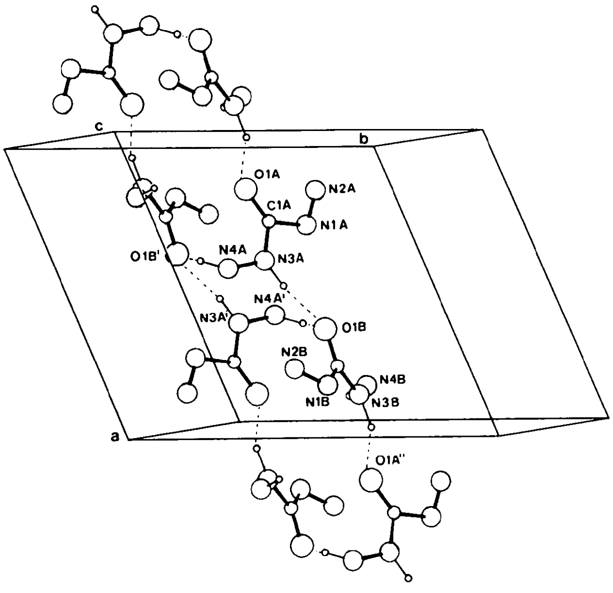

Fig. 2. Packing of the molecules. Hydrogen bonds are shown with broken lines. Phenyl rings are omitted for clarity.

Table 5. *Hydrogen bonds* (*distances in* Å, *angles in degrees*)

N(3*A*)···O(1*B*)	3·066 (16)	N(3*A*)–H(N3*A*)···O(1*B*)	155·5 (3)
N(4*A*)···O($1B^{i}$)	2·920 (11)	N(4*A*)–H(N4*A*)···O($1B^{i}$)	143·6 (3)
N(3*B*)···O($1A^{ii}$)	2·850 (17)	N(3*B*)–H(N3*B*)···O($1A^{ii}$)	145·0 (3)

H(N3*A*)···O(1*B*)	2·155 (12)
H(N4*A*)···O($1B^{i}$)	2·014 (6)
H(N3*B*)···O($1A^{ii}$)	1·944 (15)

Symmetry code

None	x,	y,	z
(i)	$1-x$,	$1-y$,	$1-z$
(ii)	$1+x$,	y,	z

phenyl group of the azo chain is rather coplanar. This alternating position of the phenyl rings *versus* the N—CO—N groups gives the convenient packing within the cell.

From this structure determination it is deduced that in the solid state DPCO exists only in the keto form, that the molecule is nonplanar and that no intramolecular but only intermolecular N—H···O bonds are present.

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References

BLATON, N., PEETERS, O., WILLEMS, G. & DE RANTER, C. (1977). *Cryst. Struct. Commun.* **6**, 603–609.

BURKE-LAING, M. & LAING, M. (1976). *Acta Cryst.* B**32**, 3216–3224.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **24**, 321–324.

CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, edited by J. S. ROLLETT, pp. 112–116. Oxford: Pergamon Press.

DE RANTER, C. J., BLATON, N. M. & PEETERS, O. M. (1979). *Acta Cryst.* B**35**, 1295–1297.

DOMIANO, P., PELLINGHELLI, M. A. & TIRIPICCHIO, A. (1972). *Acta Cryst.* B**28**, 2495–2498.

International Tables for X-ray Crystallography (1968). Vol. III, pp. 275–277. Birmingham: Kynoch Press.

KEMULA, W. & JANOWSKI, A. (1966). *Rocz. Chem.* **40**, 9–20.

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN* 74, *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain-la-Neuve, Belgium.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., pp. 232–240. Ithaca: Cornell Univ. Press.

STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The XRAY system – version of June 1972. Tech. Rep. TR-192. Computer Science Center, Univ. of Maryland, College Park, Maryland.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

WILLEMS, G. J., BLATON, N. M., PEETERS, O. M. & DE RANTER, C. J. (1977). *Anal. Chim. Acta*, **88**, 345–352.

WILLEMS, G. J. & DE RANTER, C. J. (1974). *Anal. Chim. Acta*, **68**, 111–118.

WILLEMS, G. J. & ZEEGERS-HUYSKENS, TH. (1976). *Rocz. Chem.* **50**, 1973–1985.

Acta Cryst. (1979). B35, 2634–2638

Empilement Cristallin et Séparation Spontanée des Enantiomères. Structure Cristalline de la *N*-Acétyl-DL-méthionine-diéthylamide

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Abstract

N-Acetyl-DL-methionine-diethylamide (AMDE) and *N*-acetyl-DL-methionine-methylethylamide (AMME) display very similar crystal parameters and both crystallize in space group $P2_1/c$. The crystal structure of AMDE was solved by *MULTAN* and refined by least-squares methods to $R = 0{\cdot}046$ [$C_{11}H_{22}N_2O_2S$; $M_r = 246$; $a = 9{\cdot}357\,(2)$, $b = 19{\cdot}763\,(2)$, $c = 8{\cdot}256\,(2)$ Å, $\beta = 115{\cdot}15\,(3)°$; $d_{\text{calc}} = 1{\cdot}18$ Mg m^{-3}; $Z = 4$]. Hetero-

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