

## References

- BAK, B., HANSEN-NYGAARD, L. & RASTRUP-ANDERSEN, J. (1958). *J. Mol. Spectrosc.* **2**, 361–368.
- BAR, I. & BERNSTEIN, J. (1977). *Acta Cryst.* **B33**, 1738–1744.
- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.
- BERNSTEIN, J. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 946–950.
- BERNSTEIN, J. & IZAK, I. (1976). *J. Chem. Soc. Perkin Trans. 2*, pp. 429–434.
- BERNSTEIN, J. & SCHMIDT, G. M. J. (1972). *J. Chem. Soc. Perkin Trans. 2*, pp. 951–955.
- BREGMAN, J., LEISEROWITZ, L. & OSAKI, K. (1964). *J. Chem. Soc.* pp. 2086–2100.
- BREGMAN, J., LEISEROWITZ, L. & SCHMIDT, G. M. J. (1964). *J. Chem. Soc.* pp. 2068–2085.
- BÜRGI, H. B. & DUNITZ, J. D. (1970). *Helv. Chim. Acta*, **53**, 1747–1764.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.
- COCHRAN, W. (1953). *Acta Cryst.* **6**, 260–268.
- COHEN, M. D., SCHMIDT, G. M. J. & FLAVIAN, S. (1964). *J. Chem. Soc.* pp. 2041–2051.
- DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* **A24**, 390–397.
- HADJODIS, E. & XEXAKIS, J. (1976). Abstr. 6th IUPAC Symp. Photochem. July 19–23, 1976, Aix-en Provence, France, pp. 121–124.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- LONG, R. E. (1965). PhD Thesis. Univ. of California, Los Angeles.
- NAKAI, H., SHIRO, M., EZUMI, K., SAKATA, S. & KUBOTA, T. (1976). *Acta Cryst.* **B32**, 1827–1833.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- OLOVSSON, I. & JÖNSSON, P.-G. (1976). *The Hydrogen Bond*. Edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, Vol. II, pp. 401–402. Amsterdam: North-Holland.
- OTTERSEN, T. & SEFF, K. (1974). *Acta Cryst.* **B30**, 955–959.
- PAULING, L. (1960). *The Nature of the Chemical Bond*. 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
- PERAHIA, D. & PULLMAN, A. (1973). *Chem. Phys. Lett.* **19**, 73–75.
- POPLE, J. A. & BEVERIDGE, D. L. (1970). *Approximate Molecular Orbital Theory*. New York: McGraw-Hill.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- SUNDARALINGAM, M. & JENSEN, L. H. (1965). *Acta Cryst.* **18**, 1053–1058.
- VANDLEN, R. L. & TULINSKY, A. (1971). *Acta Cryst.* **B27**, 437–442.
- VOGEL, A. I. (1966). *Practical Organic Chemistry*, pp. 653–654. London: Longmans.
- WILSON, A. J. C. (1942). *Nature (London)*, **150**, 151–152.
- WYCKOFF, H. W., DOSCHER, M., TSENOGLOU, D., INAGAMI, T., JOHNSON, L. N., HARDMAN, K. D., ALLEWEL, N. M., KELLY, D. M. & RICHARDS, F. M. (1967). *J. Mol. Biol.* **27**, 563–578.

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## Two Crystal Structures of a Cyclic Diacetylene, C<sub>21</sub>H<sub>14</sub>O<sub>4</sub>

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*o,o'*-Diacetylenyldiphenyl glutarate (BPG) [systemic name: 16,17,18,19-tetrahydro-8,9-dihydro-6*H*-dibenzo[*h,n*][1,7]dioxacyclotadecin-6,10(7*H*)-dione] crystallizes in two modifications. Modification 1 is monoclinic, *C2/c*, *a* = 22.66 (10), *b* = 7.88 (2), *c* = 9.85 (5) Å, β = 108.0(5)°, *D<sub>x</sub>* = 1.31 Mg m<sup>-3</sup> (at 120 K), *Z* = 8. Modification 2 is monoclinic, *P2<sub>1</sub>/n*, *a* = 21.680 (20), *b* = 13.830 (9), *c* = 5.420 (2) Å, β = 90.17 (6)°, *D<sub>x</sub>* = 1.35 Mg m<sup>-3</sup>, *Z* = 4. The structures have been refined to *R* = 0.078 (752 observed reflections) and 0.062 (2982 observed reflections) for modifications 1 and 2, respectively. The different reactivity in the solid state of the two forms can be explained by the different packing of the diacetylene groups.

### Introduction

Many substituted diacetylenes undergo solid-state polymerization by 1:4 addition of adjacent molecules (Wegner, 1972). Topochemical polymerization is initiated by annealing or exposure to UV, X-rays or γ-

rays and leads to polymers containing fully conjugated polymer chains. In this way large, nearly defect-free polymer single crystals can be obtained. The solid-state reactivity has been found to depend only on the packing of the monomer molecules and not on the chemical nature of the substituents. The title com-

pound, in the following abbreviated BPG, crystallizes in two forms, one of which (modification 1) is reactive in the solid state while the other is not. Cyclic diacetylenes like BPG are of special interest because, depending on the relative orientation of the ester linkage in neighboring monomers, two different stereoregular polymers can be obtained (Fig. 1). Cell dimensions suggest that the polymer obtained from modification 1 is of type *B* in Fig. 1 (Baughman & Yee, 1974). This assumption has been confirmed by a structure analysis of a polymer-monomer solid solution (Day & Lando, 1978). The aim of this study was to gain more information on the complex relationship between molecular packing and reactivity in the crystalline state.

### Experimental

BPG crystallizes from acetone-hexane (50:50) in modification 1 as colorless plates which rapidly turn red upon exposure to light. The space group and preliminary cell dimensions were determined from single-crystal photographs. For intensity collection the monomer crystals were cut to  $0.5 \times 0.2 \times 0.2$  mm. The intensities were recorded by multiple-film equi-inclination Weissenberg photographs with Ni-filtered Cu  $K\alpha$  radiation for layers 0 to 7 about *b* and 0 to 9 about *c*. During data collection the temperature was maintained at about 120 K by a low-temperature attachment. This prevents polymerization of the reactive monomer in the X-ray beam. For each photograph a new crystal was chosen. Cell dimensions at 120 K were determined from Straumanis-type double-radius Weissenberg photographs ( $R = 57.3$  mm). 934 independent reflections were observed ( $\sin \theta < 0.65$ ) of which 182 were considered to have intensities below a threshold value. They were assigned half the threshold value of the observable intensity and were given zero weight during the refinement. Intensities were estimated visually. The  $F^2$  values corrected for Lorentz and polarization effects from the various sets of photo-

graphs were correlated by an averaging process. The scale factors were allowed to vary during the refinement. No absorption correction was applied.

Crystals of modification 2 were obtained from ethanol solution by slow evaporation. A specimen  $0.4 \times 0.1 \times 0.2$  mm was chosen. Intensities were collected on a Nonius automatic four-circle diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. The  $\theta$ - $2\theta$  scan mode was used. Of the 4586 accessible unique reflections significant counts were recorded for 2982 ( $2\theta < 60^\circ$ ). Cell dimensions were computed from the setting angles of 15 automatically centered reflections. The space group  $P2_1/n$  was determined from the systematic absences  $0k0$  for *k* odd and  $h0l$  for *h* + *l* odd.

### Structure determination

The crystal structure of modification 2 was solved with *MULTAN* (Declercq, Germain, Main & Woolfson, 1973). For modification 1 the coordinates given by Day & Lando (1978) for the monomer in the monomer-polymer solid solution were used as starting values for the refinement. Refinement was by a full-matrix least-squares method. Unit weights were used throughout. The coordinates of all H atoms were found in difference maps. In the refinement of modification 1 the parameters of the H atoms were not varied. For modification 2 all positional parameters were refined with anisotropic thermal motion for the non-hydrogen atoms and fixed isotropic thermal motion for the H atoms. Final *R* indices were 0.078 and 0.062, respectively. The programs used were those of the XRAY 76 system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) and the plotting program *ORTEP* (Johnson, 1965). Scattering factors for the non-hydrogen atoms were from *International Tables for X-ray Crystallography* (1968) and for H from Stewart, Davidson & Simpson (1965).

An attempt to refine modification 1 in space group *Cc* gave essentially the same parameters as for *C2/c* but there was a high correlation between matrix elements. In addition, the values of  $\langle |E^2 - 1| \rangle$  and  $\langle |E| \rangle$  indicated the structure to be centrosymmetric. The final atomic parameters and (for H only) thermal parameters are given in Table 1.\*

### Discussion

Bond lengths and angles of the two forms are given in Fig. 2. The ring containing the diyne system is con-

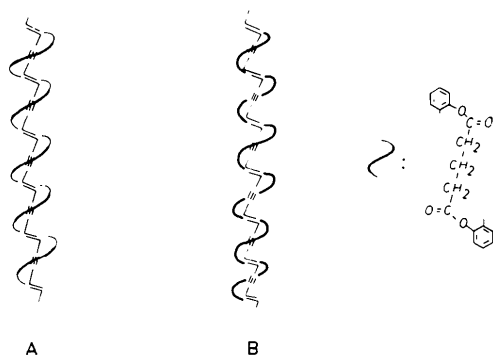


Fig. 1. Two possible isomeric polymers of the cyclic diacetylene BPG.

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33880 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final atomic parameters* ( $\times 10^4$ ) and, for H atoms, *isotropic thermal parameters*

	E.s.d.'s are given in parentheses.			
	x	y	z	B ( $\text{\AA}^2$ )
<i>(a) Modification 1</i>				
C(1)	5233 (3)	-318 (9)	8168 (8)	
C(2)	5652 (4)	-111 (10)	9353 (9)	
C(3)	6132 (3)	171 (11)	10715 (8)	
C(4)	6507 (4)	-1139 (11)	11562 (8)	
C(5)	6977 (3)	-808 (11)	12888 (9)	
C(6)	7078 (3)	849 (12)	13418 (8)	
C(7)	6723 (3)	2224 (11)	12610 (8)	
C(8)	6248 (3)	1855 (11)	11302 (8)	
C(9)	6025 (3)	4127 (10)	9558 (8)	
C(10)	5496 (4)	5196 (10)	8610 (9)	
C(11)*	5000	4108 (12)	7500	
O(1)	5840 (2)	3145 (7)	10517 (5)	
O(2)	6561 (2)	4052 (8)	9500 (6)	
H(1)	6394	-2434	11061	3.0
H(2)	7341	-1870	13571	3.0
H(3)	7479	1013	14482	3.0
H(4)	6735	3405	13022	3.0
H(5)	5702	6141	8163	3.0
H(6)	5292	5923	9144	3.0
H(7)	4802	3108	7958	3.0
<i>(b) Modification 2</i>				
C(1)	443 (1)	6687 (2)	597 (5)	
C(2)	1056 (2)	6692 (2)	1240 (6)	
C(3)	1471 (1)	6192 (3)	-227 (6)	
C(4)	1273 (2)	5716 (3)	-2292 (7)	
C(5)	657 (2)	5703 (3)	-2918 (6)	
C(6)	226 (1)	6190 (2)	-1457 (6)	
C(7)	-208 (2)	8004 (3)	1412 (7)	
C(8)	-718 (2)	8332 (3)	3103 (7)	
C(9)	-1307 (2)	7886 (4)	1994 (8)	
C(10)	-1897 (2)	8179 (3)	3159 (7)	
C(11)	-2396 (2)	7801 (3)	1467 (7)	
C(12)	-3022 (1)	6446 (2)	633 (6)	
C(13)	-3643 (2)	6409 (3)	1257 (6)	
C(14)	-4042 (1)	5893 (3)	-220 (7)	
C(15)	-3833 (2)	5411 (3)	-2260 (7)	
C(16)	-3211 (2)	5442 (3)	-2875 (6)	
C(17)	-2798 (1)	5963 (2)	-1421 (6)	
C(18)	-2151 (2)	6001 (2)	-1955 (6)	
C(19)	-1604 (2)	6041 (2)	-2195 (6)	
C(20)	-969 (2)	6098 (2)	-2204 (6)	
C(21)	-422 (2)	6145 (2)	-1960 (6)	
O(1)	19 (1)	7173 (2)	2161 (4)	
O(2)	33 (1)	8418 (2)	-384 (6)	
O(3)	-2573 (1)	8192 (2)	-323 (5)	
O(4)	-2614 (1)	6918 (2)	2224 (4)	
H(1)	1202 (15)	7052 (24)	2668 (61)	4.0
H(2)	1871 (16)	6168 (24)	314 (59)	4.0
H(3)	1538 (15)	5336 (25)	-3139 (61)	4.0
H(4)	519 (15)	5385 (25)	-4363 (62)	4.0
H(5)	-612 (14)	8089 (23)	4998 (56)	4.0
H(6)	-680 (14)	9085 (23)	3125 (60)	4.0
H(7)	-1297 (14)	8155 (23)	98 (56)	4.0
H(8)	-1294 (14)	7046 (23)	2312 (56)	4.0
H(9)	-1920 (14)	7843 (23)	4947 (56)	4.0
H(10)	-1836 (14)	9048 (23)	3180 (56)	4.0
H(11)	-3765 (14)	6747 (22)	2681 (56)	4.0
H(12)	-4486 (14)	5830 (23)	567 (59)	4.0
H(13)	-4106 (14)	5045 (23)	-3388 (57)	4.0
H(14)	-3060 (14)	5089 (22)	4280 (57)	4.0

\* Atom C(11) in modification 1 is in a special position of symmetry 2.

considerably strained as shown by the strong bending of the diacetylene group which is observed in both structures. In the reactive form 1 the molecule occupies a position of symmetry 2. As a consequence of this additional constraint on the ring conformation the bending is restricted to the plane of the phenyl rings. In addition, the triple bonds are lengthened. In modification 2 the bending of the diacetylene group is observed in a direction perpendicular to the plane of the phenyl rings. In both structures the phenyl rings are planar within experimental error. The angle between the phenyl rings in modification 2 is  $17.5^\circ$ . Stereoscopic views of both structures are shown in Figs. 3 and 4.

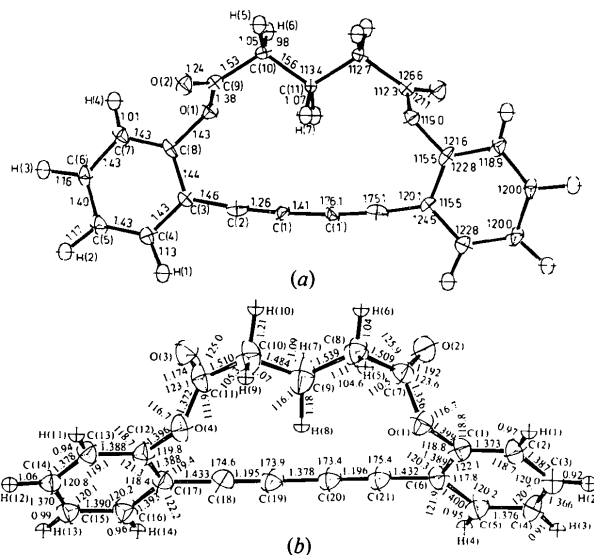


Fig. 2. Observed bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ). The 50% probability ellipsoids are shown. *(a)* Modification 1. The e.s.d.'s of bond lengths are typically  $0.01 \text{\AA}$ , of bond angles  $0.6\text{--}0.8^\circ$ . *(b)* Modification 2. The e.s.d.'s of bond lengths are typically  $0.004\text{--}0.005 \text{\AA}$  (of bonds to H atoms  $0.03 \text{\AA}$ ), of bond angles  $0.3\text{--}0.4^\circ$ .

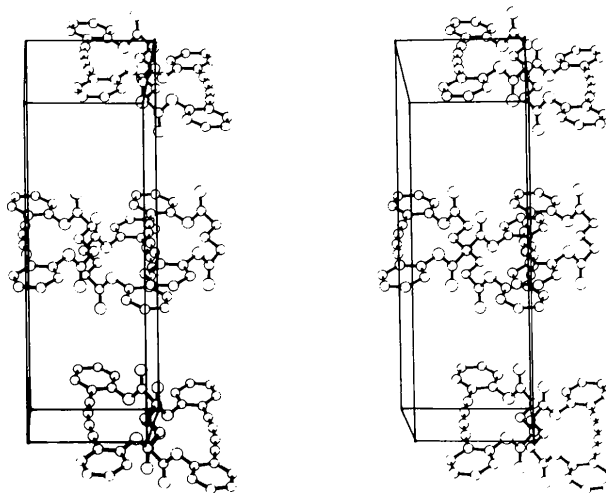
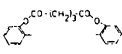







Fig. 3. Stereoscopic view of modification 1. *a* is vertical and *b* horizontal.

Table 2. Packing parameters for some diacetylene monomers  $R_1-C\equiv C-C\equiv C-R_2$ 

$R_1$	$R_2$	$d_1$ (Å)	$\varphi_1$ (°)	Reactivity	Reference
	$= R_1$	4.93	46	+*	
		5.42	90	- <sup>†</sup>	
	$= R_1$	5.11	44	+§	Enkelmann & Wegner (1977)
		46	46	-	
	$= R_1$	5.03	67	-	Mayerle & Clarke (1978)
$-CH_2OH$	$= R_1$	4.76	41	+*	Hädicke, Penzien & Schnell (1971)
$-CH_2OH$	$-CH_3$	4.87	49.6	+*	Fisher, Batchelder & Hursthouse (1978)
	$= R_1$	4.66	90	-	Mayerle & Flandera (1978)
	$= R_1$	4.55	60	+†	Enkelmann, Schleier, Wegner, Eichele & Schworer (1977)
	$= R_1$	4.35	61.5	-	Enkelmann (1978)
$-CH_2O-$	$= R_1$	8.53	77	-	Morosin & Harrah (1977)
		7.47	73	- <sup>¶</sup>	
$-CH_2O-CO-$	$= R_1$	4.35	58	(+) <sup>‡</sup> <sup>¶</sup>	Hanson (1975)
		8.48	40	-	

\* No complete conversion.

† Phase transition during polymerization.

‡ Reactive under pressure.

§ Two independent molecules.

¶ Two modifications.

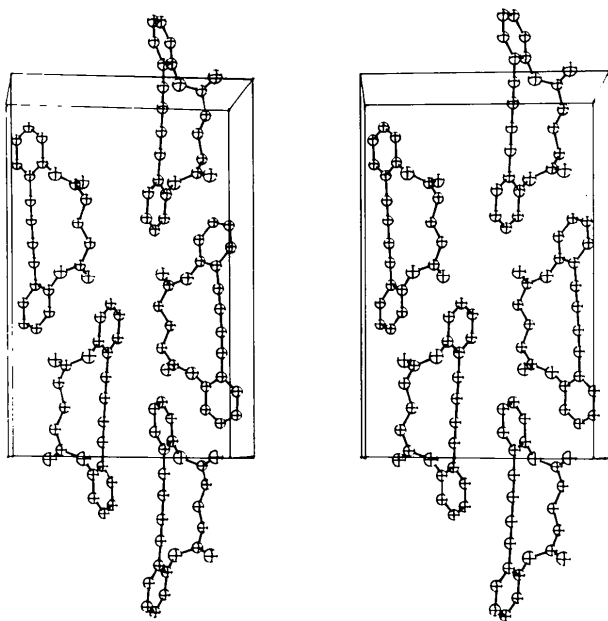


Fig. 4. Stereoscopic view of modification 2. a is vertical and b horizontal.

The bending of the diacetylene group has no influence on the reactivity in the solid state which is completely controlled by the monomer packing. The arrangement of neighboring diacetylene groups can be described by two parameters, the stacking distance  $d_1$  and the angle  $\varphi_1$  between the diacetylene group and the stacking axis (Fig. 5). The optimal packing conditions

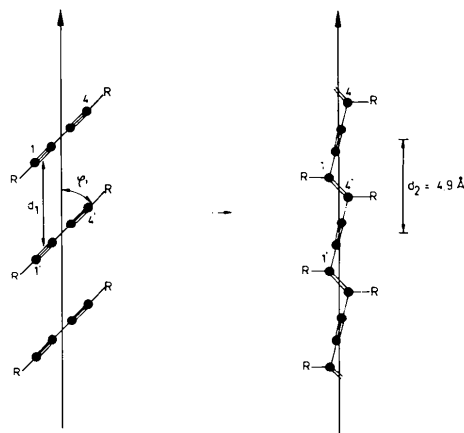


Fig. 5. Packing parameters for diacetylenes.

necessary to bring about reactivity,  $d_1 \approx 5 \text{ \AA}$  and  $\varphi_1 \approx 45^\circ$ , have been derived by Baughman (1974) from models. However, until recently no crystal structures of active diacetylene monomers were known since they polymerize extremely rapidly in the X-ray beam. This difficulty can be overcome by collecting the data at low temperatures (Enkelmann & Wegner, 1977). The packing parameters of the two forms of BPG and of some other diacetylene monomers are given in Table 2 which shows that the reactivity of diacetylenes in the solid state can be fairly well described in terms of the packing parameters  $d_1$  and  $\varphi_1$ . However, knowledge of the size and chemical nature of the substituents gives no basis for predicting the monomer structure.

Although in the active BPG modification the neighboring monomers are stacked along *c* in an arrangement which should be most favorable for solid-state reactivity, the conversion to polymer is never complete. The residual monomer can be extracted leaving very disordered almost fiber-like crystals of the pure polymer. The low reactivity of BPG can be attributed to the fact that the phenyl rings are fixed directly to the diyne system. This restricts the mobility of the side groups which seems to be necessary for a fast and complete polymerization.

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#### References

- BAUGHMAN, R. H. (1974). *J. Polym. Sci. Polym. Phys. Ed.* **12**, 1511–1535.  
 BAUGHMAN, R. H. & YEE, K. C. (1974). *J. Polym. Sci. Polym. Chem. Ed.* **12**, 2467–2475.  
 DAY, D. & LANDO, J. B. (1978). *J. Polym. Sci. Polym. Phys. Ed.* **16**, 1009–1022.

- DECLERCQ, J. P., GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1973). *Acta Cryst. A* **29**, 231–234.  
 ENKELMANN, V. (1978). Unpublished results.  
 ENKELMANN, V., SCHLEIER, G., WEGNER, G., EICHELE, H. & SCHWOERER, M. (1977). *Chem. Phys. Lett.* **12**, 314–319.  
 ENKELMANN, V. & WEGNER, G. (1977). *Angew. Chem.* **89**, 432; *Angew. Chem. Int. Ed. Engl.* **16**, 416.  
 FISHER, D. A., BATCHELDER, D. N. & HURSTHOUSE, M. B. (1978). *Acta Cryst. B* **34**, 2365–2367.  
 HÄDICKE, E., PENZIEN, K. & SCHNELL, H. W. (1971). *Angew. Chem.* **83**, 1024.  
 HANSON, A. W. (1975). *Acta Cryst. B* **31**, 831–834.  
*International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed. Birmingham: Kynoch Press.  
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.  
 MAYERLE, J. J. & CLARKE, T. C. (1978). *Acta Cryst. B* **34**, 143–147.  
 MAYERLE, J. J. & FLANDERA, M. A. (1978). *Acta Cryst. B* **34**, 1374–1376.  
 MOROSIN, B. & HARRAH, L. (1977). *Acta Cryst. B* **33**, 1760–1764.  
 STEWART, J. M., MACHIN, P. A., DICKINSON, C., AMMON, H. L., HECK, H. & FLACK, H. (1976). The XRAY 76 system. Tech. Rep. TR-446. 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.  
 WEGNER, G. (1972). *Makromol. Chem.* **154**, 35–48.

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## The Neutron Crystal Structure at $-75^{\circ}\text{C}$ of Polymorph II of 5,5-Diethylbarbituric Acid (Barbital)

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Polymorph II of barbital ( $\text{C}_8\text{H}_{12}\text{N}_2\text{O}_3$ ) at  $-75^{\circ}\text{C}$  is monoclinic, space group  $C2/c$  with X-ray ( $\text{Mo } K\alpha$ ) lattice parameters  $a = 7.113$  (2),  $b = 14.103$  (3),  $c = 9.745$  (1) Å,  $\beta = 88.86$  (3) $^{\circ}$  and with four molecules in the unit cell. Intensities for 1369 neutron reflections with  $\sin \theta/\lambda < 0.71$  Å $^{-1}$  ( $\lambda = 1.0470$  Å) were used in a structure refinement which converged at  $R(F^2) = 0.053$ . The room-temperature X-ray structure is confirmed. In the  $-\text{CO}-\text{NH}-\text{CO}-$  system, 0.015 Å differences within pairs of CO and CN bond lengths become significant because of the better precision in the neutron structure. There is intramolecular motion in the ethyl groups where r.m.s. amplitudes up to 0.4 Å are observed for the H atoms.

#### Introduction

The crystal structure determination of polymorph II of 5,5-diethylbarbituric acid (barbital) using neutron and

X-ray diffraction has been undertaken in order to analyze the electronic charge-density distribution. Barbital is chemically the simplest drug-active barbiturate. Of the three polymorphs of barbital for which