MAIN, P., WOOLFSON, M. M. & GERMAIN, G. (1971). MULTAN. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data. Univs. of York, England, and Louvain, Belgium.

MARSH, R. E. & DONOHUE, J. (1967). Adv. Protein Chem. 22, 235–256.

VALENTE, E. J., HISKEY, R. G. & HODGSON, D. J. (1979). Biochim. Biophys. Acta, 579, 446–468.

WRIGHT, W. B. (1958). Acta Cryst. 11, 632–653.

Diglycidyl Ether of Bisphenol A (DGEBA)*

By Judith L. Flippen-Anderson and Richard Gilardi

Laboratory for the Structure of Matter, Naval Research Laboratory, Washington, DC 20375, USA

Abstract. $C_{21}H_{24}O_4$, monoclinic, $P2_1/c$, $a = 8.260$ (4), $b = 11.659$ (4), $c = 20.228$ (6) Å, $\beta = 105.6$ (1)°, $Z = 4$, $d_c = 1.205$ (1) Mg m^{-3}. The structure was solved by the symbolic addition procedure and refined, using 2453 reflections, to an R_w of 0.055. The epoxide ring on one end of the molecule is disordered.

Introduction. DGEBA is the monomer of one of the most commonly used epoxy resins. It can be cured with piperidine. One curing mechanism, as determined by NMR is
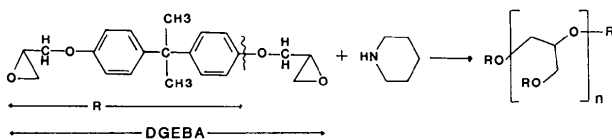
(Sojka & Moniz, 1976). Crystals used in the X-ray analysis were provided by A. N. Garroway of the Chemistry Division of the Naval Research Laboratory. The crystals were prepared by sublimation from a melt of DER 332 (Dow Chemical). The melting point was determined to be 315–315.5 K. The crystals were extremely large (2–10 mm dimensions) and quite soft. Data were collected on an irregularly shaped fragment which had been chipped off the corner of one of the parent crystals. Cell dimensions were determined from a least-squares refinement of 18 independently measured reflections. Data were collected on a Nicolet P3F diffractometer using Cu $K\alpha$ radiation with a graphite monochromator on the incident beam. The θ–2θ scan technique was used to measure the intensities of 2453 independent reflections out to $2\theta_{max} = 112°$.

The structure was solved by routine application of the symbolic addition procedure (Karle & Karle, 1966). Atomic scattering factors used for the least-

---

* 2,2'-[4,4'-Isopropylidenebis(phenoxymethyl)]bisoxiran.

squares refinement were those listed in *International Tables for X-ray Crystallography* (1962) and the function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1.0$. All data were used in the full-matrix least-squares refinement (Busing et al., 1975). It became obvious after only a few cycles of refinement that the structure was not complete. A difference map computed at this point indicated a disorder at one end of the molecule.

It should be mentioned at this point that the disorder was suspect when it first appeared and the possibility of an ordered structure in space group $P2_1$ was explored. The disorder appeared in the $P2_1$ cell as well and the refinement was thus continued in the original $P2_1/c$ cell.

The disorder consists of two alternative orientations for the epoxide ring connected to C(22). However, both alternatives have one atomic position in common, labelled $A(24)$. One epoxide alternative consists of C(23), $A(24)$ and O(25). The other alternative, approximately equally favored, contains C(23'), $A(24)$ and C(25'). Occupancies for the four split atomic sites were set at 0.5 and not varied. The parameters of only one alternative were refined in any particular cycle; atom $A(24)$ remained unresolved in difference Fourier maps and was treated as if it were a single atom during refinement. All atoms of the disordered epoxide rings were considered to be C atoms until the refinement was nearly complete. H atoms on the ordered portion of the molecule were found in a difference map computed after some anisotropic refinement had been performed. H coordinates were varied in the ensuing cycles but their thermal parameters were set equal to the final isotropic values for the atoms to which they were bonded and held constant. Under these conditions the refinement converged at $R_w = 0.081$ where $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. At this point atom 25 was converted to an O because it had an intermolecular approach to a neighboring C atom of 3.18 (1) Å. This change reduced R_w to 0.069. The

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3} \sum_i \sum_j \beta_{ij} \, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	*y*	*z*	B_{eq} (Å²)
C(1)	0·9201 (4)	−0·1950 (3)	0·7352 (2)	4·7 (1)
C(2)	0·8749 (4)	−0·1021 (3)	0·6785 (2)	4·4 (1)
C(3)	0·7079 (5)	−0·0700 (3)	0·6523 (2)	5·3 (1)
C(4)	0·6599 (5)	0·0130 (3)	0·6025 (2)	5·7 (1)
C(5)	0·7803 (4)	0·0668 (3)	0·5770 (2)	4·7 (1)
C(6)	0·9458 (5)	0·0377 (3)	0·6018 (2)	5·1 (1)
C(7)	0·9926 (4)	−0·0474 (3)	0·6527 (2)	5·0 (1)
C(8)	0·8026 (4)	−0·2973 (3)	0·7124 (2)	4·4 (1)
C(9)	0·8093 (4)	−0·3593 (3)	0·6549 (2)	4·6 (1)
C(10)	0·7070 (4)	−0·4525 (3)	0·6308 (2)	4·6 (1)
C(11)	0·5914 (4)	−0·4865 (3)	0·6651 (2)	4·5 (1)
C(12)	0·5811 (5)	−0·4257 (3)	0·7226 (2)	6·2 (1)
C(13)	0·6840 (5)	−0·3337 (3)	0·7454 (2)	6·1 (1)
C(14)	0·8350 (5)	0·2025 (4)	0·4966 (2)	6·2 (1)
C(15)	0·7422 (6)	0·2922 (4)	0·4491 (2)	6·5 (1)
C(16)	0·8311 (6)	0·3920 (4)	0·4344 (3)	7·6 (2)
C(17)	0·8999 (6)	−0·1400 (4)	0·8021 (2)	6·5 (1)
C(18)	1·1025 (5)	−0·2354 (4)	0·7488 (2)	5·9 (1)
O(19)	0·7186 (3)	0·1485 (2)	0·5272 (1)	6·1 (1)
O(20)	0·7273 (4)	0·3992 (2)	0·4800 (2)	8·7 (1)
O(21)	0·4840 (3)	−0·5773 (2)	0·6461 (2)	5·5 (1)
C(22)	0·4887 (6)	−0·6385 (4)	0·5849 (2)	6·0 (1)
C(23)	0·3777 (11)	−0·7371 (7)	0·5774 (4)	5·8 (3)
A(24)	0·3021 (5)	−0·7856 (4)	0·5092 (2)	8·1 (3)
O(25)	0·2119 (7)	−0·7064 (5)	0·5431 (4)	8·7 (2)
C(23')	0·3069 (10)	−0·6900 (6)	0·5536 (4)	5·4 (3)
C(25')	0·2958 (9)	−0·8078 (5)	0·5787 (3)	3·8 (2)

Table 2. *Hydrogen coordinates*

	x	*y*	*z*
H(3)	0·621 (5)	−0·113 (4)	0·664 (2)
H(4)	0·535 (5)	0·025 (4)	0·576 (2)
H(6)	1·031 (5)	0·076 (4)	0·591 (2)
H(7)	1·113 (5)	−0·058 (4)	0·676 (2)
H(9)	0·886 (5)	−0·332 (3)	0·631 (2)
H(10)	0·710 (5)	−0·488 (3)	0·587 (2)
H(12)	0·496 (5)	−0·449 (4)	0·743 (2)
H(13)	0·676 (5)	−0·293 (4)	0·783 (2)
H(14)	0·880 (6)	0·150 (4)	0·476 (2)
H(14)	0·938 (5)	0·243 (4)	0·539 (2)
H(15)	0·632 (6)	0·267 (4)	0·407 (2)
H(16)	0·770 (6)	0·427 (4)	0·389 (2)
H(16)	0·966 (6)	0·396 (4)	0·466 (2)
H(17)	0·948 (5)	−0·195 (4)	0·842 (2)
H(17)	0·791 (6)	−0·111 (4)	0·794 (2)
H(17)	0·983 (5)	−0·073 (4)	0·813 (2)
H(18)	1·185 (5)	−0·176 (4)	0·770 (2)
H(18)	1·125 (5)	−0·298 (4)	0·785 (2)
H(18)	1·130 (5)	−0·268 (4)	0·709 (2)
H(22)	0·601 (5)	−0·679 (4)	0·597 (2)
H(22)	0·469 (5)	−0·583 (4)	0·546 (2)
H(23)	0·385 (13)	−0·778 (8)	0·599 (5)
H(24)	0·353 (10)	−0·766 (7)	0·454 (4)
H(24)	0·273 (10)	−0·896 (8)	0·500 (4)
H(23')	0·228 (12)	−0·650 (9)	0·539 (5)
H(25')	0·373 (11)	−0·794 (7)	0·610 (4)
H(25')	0·238 (11)	−0·810 (7)	0·586 (4)

intramolecular distances and angles for the second disordered ring consistently indicated that its O atom lies at the position labelled $A(24)$. This position is thus occupied partially by C and partially by O atoms. Therefore, atom 24 was assigned a nitrogen scattering factor for the rest of the refinement, which reduced R_w to 0·065. H atoms on the disordered atoms were put in at calculated positions, since they did not appear in difference maps and their positional coordinates were refined. A final round of refinement cycles lowered R_w to 0·055. The final conventional R value $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ was 0·066. At the end of the refinement the standard deviation of an observation of unit weight was 1·60 and a difference map calculated at that point showed a maximum absolute density of 0·271. Refined coordinates and B_{eq} values for the heavy atoms are listed in Table 1. H coordinates are listed in Table 2.*

Discussion. The stereoconfiguration of DGEBA is illustrated in Fig. 1. One might expect this molecule to exhibit twofold symmetry and indeed there is a non-crystallographic twofold rotation axis which passes through C(1) and relates the two sides of the molecule up to O(19) and O(21).

The pseudosymmetry deteriorates beyond this point, regardless of which epoxide alternative is chosen at the O(21) end of the molecule. This is undoubtedly due to the quite different packing environments seen at the two ends of DGEBA. At the ordered end, O(20) is located 2·57 Å from a neighboring H atom. The disordered end appears to be more crowded: O(25) to H(14) is only 2·32 Å and C(25') to H(6) is only 2·64 Å (both about 0·2 Å less than the usual van der Waals distances). Atoms C(15), C(23) and C(23') are chiral centers and, in the reported molecule, all have (S)-type chirality (IUPAC, 1970). At the disordered end, this assignment of chirality depends upon the correct identification of the O site in the epoxide ring. Because of this disorder, an appreciable fraction of (R, S)-type molecules might be undetected. However, the data agree quite well with a crystal model containing only (S,S) and (by centro-symmetric inversion) (R,R) molecules of DGEBA.
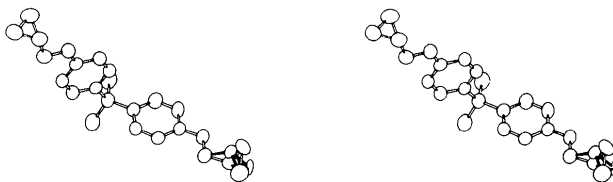
Fig. 1. Stereodiagram of DGEBA. Atoms are shown at their final refined positions. Bonds to the alternative position for the epoxide ring have been blackened.
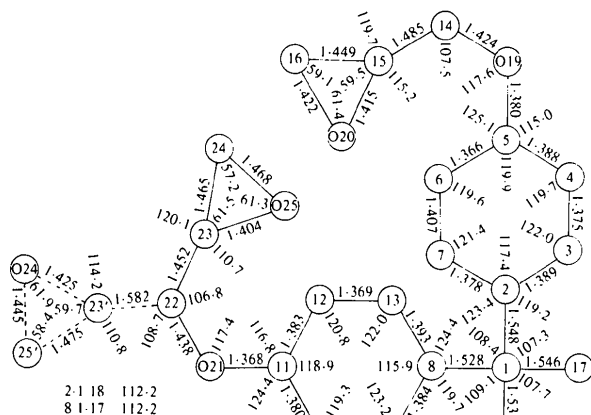
Fig. 2. Bond lengths (Å) and angles (°). For the ordered atoms standard deviations are of the order of 0·005 Å for bond lengths and 0·3° for bond angles. For disordered atoms these values are 0·008 Å and 0·6°.

Bond lengths and angles are illustrated in Fig. 2. Distances and angles in and around the epoxide rings are consistent with those found in other molecules (Foces-Foces, Cano & García-Blanco, 1977; Flippen & Karle, 1976). The CCO angle at the C which is not bonded to the remainder of the molecule is sig-

nificantly smaller than both the other epoxide angles and the CCC external angle is larger than the external CCO angle. H atoms on the disordered end of the molecule were not very well determined. For the ordered H atoms the average C—H bond length was 0·93 (4) Å with a range from 0·87 (4)–1·13 (4) Å. The molecules are held together solely by van der Waals forces. Intermolecular approaches (excluding H atoms) less than van der Waals distances are C(4)—C(24) at 3·55, C(6)—C(25') at 3·54 and C(13)—C(25') at 3·53 Å.

References

BUSING, W. R., MARTIN, K. O., LEVY, H. A., ELLISON, R. D., HAMILTON, W. G., IBERS, J. A., JOHNSON, C. K. & THIESSEN, W. E. (1975). *ORXFLS3*. Oak Ridge National Laboratory, Tennessee.

FLIPPEN, J. L. & KARLE, I. L. (1976). *Biopolymers*, 15, 1081–1092.

FOCES-FOCES, C., CANO, F. H. & GARCÍA-BLANCO, S. (1977). *Acta Cryst.* B33, 3521–3524.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

IUPAC (1970). *J. Org. Chem.* 35, 2849–2867.

KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849–859.

SOJKA, S. A. & MONIZ, W. B. (1976). *J. Appl. Polym. Sci.* 20, 1977–1982.

The Structure of 1,6-Dimethylphenazine: A Photoproduct of 2,2'-Diazido-6,6'-dimethylbiphenyl

BY YUKISHIGE KITANO

Toray Research Center Incorporated, Sonoyama, Ohtsu 520, Japan

TAMAICHI ASHIDA

Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464, Japan

AND AKIRA YABE

National Chemical Laboratory for Industry, Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan

Abstract. $C_{14}H_{12}N_2$, $M_r = 208·26$, monoclinic, $P2_1/n$, $a = 11·627$ (4), $b = 4·652$ (2), $c = 9·826$ (3) Å, $\beta = 97·95$ (4)°, $V = 526·4$ Å³, $Z = 2$, $D_m = 1·32$, $D_x = 1·314$ Mg m⁻³, μ(Mo $K\alpha$) = 0·085 mm⁻¹. The structure was solved by a direct method and refined by means of the least-squares procedure to a final R value of 0·085 for 1034 non-zero reflections collected by a four-circle diffractometer. The molecules, which have a center of symmetry, are held together by van der Waals interactions. All the atoms of the phenazine ring, together with the methyl C, lie in the same plane.

Introduction. In a study of the photolysis of organic azides, a low-temperature reaction of 2,2'-diazido-1,6-dimethylbiphenyl was undertaken (Yabe, 1980). The structures of the products were characterized by