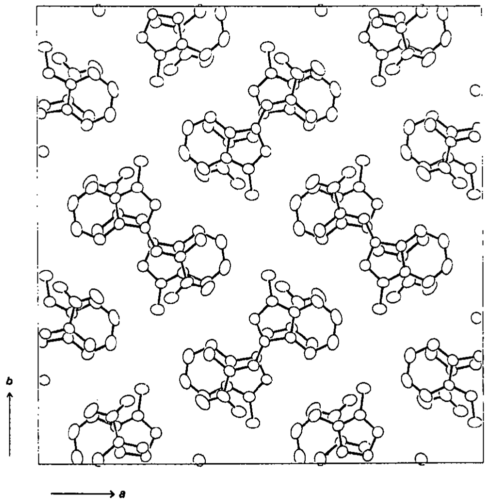

Fig. 2. Molecular packing viewed down the *xy* plane.

Although the torsion angle between the side chain and the indole nucleus reaches the value of 20·0 (4)°, the perturbation of the pyrrole ring by the polar effect of the nitro group seems to be important because the contribution of the resonance structures (4) and (5) agrees well with the observed bond lengths. Moreover, it has been suggested (Bücki & Mak, 1977) that the contribution of the resonance structure (5) is important in the resonance hybrid, since the IR absorption of the 3-(2-nitrovinyl)indoles shows several stretching C=C and C=N bands, while the polar effect of the nitro group is evidenced by the bathochromic effect of both stretching bands of this group about 1300 and 1250 $cm^{-1}$.

The deviations in the side-chain and pyrrole-ring bond distances from the normal values can be explained by taking into account the molecular packing, Fig. 2. The molecules stack up along the *c* axis forming dimers through a charge-transfer interaction between the nitrovinyl chain (acceptor) and the indole nucleus (donor), molecular zones which are parallel in the dimer (Fig. 2). The molecular overlapping in these zones gives an interplanar distance of 3·50 Å which corresponds to the values usually found for this type of charge-transfer interaction (Foster, 1973).

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# Biphenyl-2,2′-dicarboxylic Acid (Diphenic Acid)

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**Abstract.** $C_{14}H_{10}O_4$, $M_r = 242{\cdot}2$, monoclinic, $P2_1/c$, $a = 14{\cdot}032\ (3)$, $b = 11{\cdot}952\ (3)$, $c = 13{\cdot}616\ (3)$ Å, $\beta = 91{\cdot}46\ (2)°$, $V = 2282{\cdot}8\ (16)$ Å$^3$, $Z = 8$, $D_x = 1{\cdot}410$ g $cm^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 0{\cdot}97$ $cm^{-1}$, $F(000) = 1008$, $T = 296$ K, $R = 0{\cdot}064$ for 3366 observations (of 4008 unique data). The unit cell contains two independent molecules. The dihedral angles between the two ring planes are 71·3 (1)° in one molecule (*A*) and 83·6 (1)° in the other (*B*). In both molecules the carboxyl groups are located on opposite sides of the rings such that the C(2)—C(1)—C(1′)—C(2′) torsion angles are −119·3 (2)° in *A* and −106·3 (2)° in *B*.

**Introduction.** Interest in the interactions of neighboring groups on the orientation of carboxyl groups led us to examine the crystal structures of some *ortho*-substituted benzoic acids (Chiari, Fronczek, Davis & Gandour,

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1981; Fronczek, Merrill & Gandour, 1982). In a search of the Cambridge Structural Database files, we were surprised to discover that the structure of the title compound had not been determined. Further search of the literature, however, revealed that crystallographic investigation of diphenic acid predates the discovery of X-rays. Bodewig (1879) studied the morphology of diphenic acid crystals, correctly identifying their monoclinic symmetry, and measuring axial ratios and the $\beta$ angle to an accuracy of 1%. The advent of X-ray diffraction brought confusion and controversy. In 1931, in studying potentially chiral biphenyls, Clark & Pickett recorded rotation photographs of the title compound and concluded that it was orthorhombic with $Z = 8$. Huggins (1931) sharply criticized this paper for improperly using space-group theory to deduce molecular symmetry. In a fairly sarcastic reply to this criticism and to that of Pauling & Dickinson (1931), Clark (1931) admitted the possibility that diphenic acid might actually be monoclinic, $P2_1/c$. Pickett (1936) correctly determined the space group by using Weissenberg photographs.

Over 100 years after the original study, we report here the atomic positions. Our crystallographic data are comparable to the century- and half-century-old data. Because the unit cell contains two different molecules, it is understandable that few conclusions could be drawn from the limited data fifty years ago. As Professor Emeritus Pickett states in recent correspondence, 'It is very gratifying to see how techniques of the present day can unravel the mysteries of the past'.

**Experimental.** The title compound recrystallized from acetic acid, m.p. 506·6 K, crystal size 0·40 × 0·48 × 0·60 mm. Space group from systematic absences $0k0$ with $k$ odd, $h0l$ with $l$ odd; cell dimensions from setting angles of 25 reflections having $15 > \theta > 14°$. Data collected on Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation, graphite monochromator, $\omega$–$2\theta$ scans designed for $I = 50\sigma(I)$, subject to max. scan time = 180 s, scan rates varied 0·31–5·0° min$^{-1}$. Data having $1 \leq \theta \leq 25°$, $0 \leq h \leq 16$, $0 \leq k \leq 14$, $-16 \leq l \leq 16$ measured and corrected for background, Lorentz and polarization effects, no absorption correction. Three standard reflections (600, 040, 006), 2·6% maximum variation. Redundant data averaged, $R_{\text{int}} = 0{\cdot}019$. Structure solved by direct methods, using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) refined by full-matrix least squares based upon $F$, using data for which $I > 0$, weights $w = 4F_o^2[\sigma^2(I) + (0{\cdot}02F_o^2)^2]^{-1}$ using *Enraf–Nonius SDP* (Frenz & Okaya, 1980), scattering factors of Cromer & Waber (1974), anomalous-dispersion coefficients of Cromer (1974), 642 unobserved data. Non-H atoms refined anisotropically; H atoms located by $\Delta F$ synthesis and refined isotropically. Final $R = 0{\cdot}064$ [0·043 for 2599 data with $I > 3\sigma(I)$, 0·092 for all data], $wR = 0{\cdot}051$, $S = 2{\cdot}432$ for 406 variables. Max. shift $0{\cdot}04\sigma$ in the final cycle, max. residual density 0·31, min. −0·23 e Å$^{-3}$, extinction coefficient $g = 7{\cdot}9\,(6) \times 10^{-7}$ [$|F_c| = |F_o|(1 + gI_c)$].

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters*

E.s.d.'s in the least-significant digits are shown in parentheses.

| | $x$ | $y$ | $z$ | $B_{\text{eq}}$* (Å$^2$) |
|---|---|---|---|---|
| O(1*A*) | 0·47951 (9) | 0·3599 (1) | 0·18247 (9) | 4·98 (3) |
| O(2*A*) | 0·54958 (11) | 0·3769 (1) | 0·04145 (10) | 7·18 (4) |
| O(3*A*) | 0·42666 (9) | 0·0434 (1) | 0·26303 (9) | 5·08 (3) |
| O(4*A*) | 0·35008 (11) | 0·0506 (1) | 0·40252 (10) | 6·11 (4) |
| C(1*A*) | 0·49263 (13) | 0·3285 (2) | 0·09429 (13) | 3·70 (4) |
| C(2*A*) | 0·44127 (13) | 0·2281 (2) | 0·05677 (13) | 3·53 (4) |
| C(3*A*) | 0·47401 (15) | 0·1816 (2) | −0·03054 (14) | 4·57 (5) |
| C(4*A*) | 0·43225 (16) | 0·0869 (2) | −0·06944 (15) | 5·31 (6) |
| C(5*A*) | 0·35776 (15) | 0·0377 (2) | −0·02249 (15) | 5·21 (5) |
| C(6*A*) | 0·32407 (14) | 0·0833 (2) | 0·06262 (14) | 4·49 (5) |
| C(7*A*) | 0·36433 (12) | 0·1791 (2) | 0·10408 (12) | 3·38 (4) |
| C(8*A*) | 0·31322 (12) | 0·2308 (2) | 0·18800 (13) | 3·24 (4) |
| C(9*A*) | 0·26026 (13) | 0·3266 (2) | 0·16723 (13) | 3·86 (4) |
| C(10*A*) | 0·20103 (13) | 0·3733 (2) | 0·23529 (15) | 4·48 (5) |
| C(11*A*) | 0·19250 (14) | 0·3248 (2) | 0·32574 (15) | 4·82 (5) |
| C(12*A*) | 0·24630 (14) | 0·2316 (2) | 0·34954 (14) | 4·32 (5) |
| C(13*A*) | 0·30707 (12) | 0·1831 (2) | 0·28203 (13) | 3·48 (4) |
| C(14*A*) | 0·36481 (12) | 0·0865 (2) | 0·31454 (13) | 3·73 (4) |
| O(1*B*) | −0·06031 (9) | 0·3927 (1) | 0·27069 (10) | 5·36 (4) |
| O(2*B*) | −0·16314 (12) | 0·3954 (2) | 0·14715 (11) | 8·11 (5) |
| O(3*B*) | −0·02169 (9) | 0·0744 (1) | 0·32737 (9) | 4·28 (3) |
| O(4*B*) | 0·08801 (9) | 0·0562 (1) | 0·44715 (9) | 4·98 (3) |
| C(1*B*) | −0·13729 (13) | 0·3580 (2) | 0·22784 (13) | 4·01 (5) |
| C(2*B*) | −0·19548 (12) | 0·2701 (2) | 0·27363 (13) | 3·53 (4) |
| C(3*B*) | −0·27550 (14) | 0·2334 (2) | 0·21865 (14) | 4·38 (5) |
| C(4*B*) | −0·33736 (13) | 0·1566 (2) | 0·25438 (14) | 4·54 (5) |
| C(5*B*) | −0·32038 (14) | 0·1118 (2) | 0·34595 (15) | 4·60 (5) |
| C(6*B*) | −0·24116 (14) | 0·1453 (2) | 0·40082 (14) | 4·32 (5) |
| C(7*B*) | −0·17763 (12) | 0·2245 (2) | 0·36652 (13) | 3·30 (4) |
| C(8*B*) | −0·10185 (13) | 0·2641 (2) | 0·43804 (12) | 3·38 (4) |
| C(9*B*) | −0·12336 (15) | 0·3571 (2) | 0·49339 (15) | 5·11 (5) |
| C(10*B*) | −0·06325 (19) | 0·3952 (2) | 0·56907 (16) | 6·06 (6) |
| C(11*B*) | 0·01997 (16) | 0·3387 (2) | 0·59072 (15) | 5·57 (6) |
| C(12*B*) | 0·04247 (14) | 0·2466 (2) | 0·53667 (13) | 4·25 (5) |
| C(13*B*) | −0·01661 (13) | 0·2068 (2) | 0·45993 (12) | 3·36 (4) |
| C(14*B*) | 0·01550 (12) | 0·1071 (2) | 0·40641 (12) | 3·42 (4) |

* $B_{\text{eq}} = \frac{1}{3}(a^2a^{*2}B_{11} + B_{22} + c^2c^{*2}B_{33} + aca^*c^*B_{13}\cos\beta)$.

Table 2. *Distances* (Å) *and angles* (°) *for molecules A and B*

| | *A* | *B* | | *A* | *B* |
|---|---|---|---|---|---|
| O(1)–C(1) | 1·276 (2) | 1·283 (2) | O(1)–C(1)–O(2) | 121·5 (1) | 120·9 (1) |
| O(2)–C(1) | 1·233 (2) | 1·232 (2) | O(1)–C(1)–C(2) | 118·8 (1) | 120·4 (1) |
| O(3)–C(14) | 1·242 (1) | 1·247 (1) | O(2)–C(1)–C(2) | 119·7 (1) | 118·7 (1) |
| O(4)–C(14) | 1·294 (2) | 1·298 (1) | C(1)–C(2)–C(3) | 116·5 (1) | 116·1 (1) |
| C(1)–C(2) | 1·484 (2) | 1·478 (2) | C(1)–C(2)–C(7) | 123·6 (1) | 124·9 (1) |
| C(2)–C(3) | 1·401 (2) | 1·404 (2) | C(3)–C(2)–C(7) | 119·9 (1) | 119·0 (1) |
| C(2)–C(7) | 1·399 (2) | 1·394 (2) | C(2)–C(3)–C(4) | 120·6 (2) | 121·9 (1) |
| C(3)–C(4) | 1·374 (2) | 1·362 (2) | C(3)–C(4)–C(5) | 119·7 (2) | 119·4 (2) |
| C(4)–C(5) | 1·372 (2) | 1·372 (2) | C(4)–C(5)–C(6) | 120·3 (2) | 119·8 (2) |
| C(5)–C(6) | 1·375 (2) | 1·383 (2) | C(5)–C(6)–C(7) | 121·6 (2) | 122·0 (1) |
| C(6)–C(7) | 1·390 (2) | 1·389 (2) | C(2)–C(7)–C(6) | 117·9 (1) | 118·0 (1) |
| C(7)–C(8) | 1·498 (2) | 1·500 (2) | C(2)–C(7)–C(8) | 124·7 (1) | 125·0 (1) |
| C(8)–C(9) | 1·390 (2) | 1·380 (2) | C(6)–C(7)–C(8) | 116·9 (1) | 116·6 (1) |
| C(8)–C(13) | 1·406 (2) | 1·403 (2) | C(7)–C(8)–C(9) | 116·7 (1) | 116·6 (1) |
| C(9)–C(10) | 1·379 (2) | 1·392 (2) | C(7)–C(8)–C(13) | 124·7 (1) | 124·8 (1) |
| C(10)–C(11) | 1·369 (2) | 1·375 (2) | C(9)–C(8)–C(13) | 118·3 (1) | 118·3 (1) |
| C(11)–C(12) | 1·379 (2) | 1·366 (2) | C(8)–C(9)–C(10) | 121·7 (1) | 122·1 (2) |
| C(12)–C(13) | 1·396 (2) | 1·400 (2) | C(9)–C(10)–C(11) | 120·1 (2) | 119·6 (2) |
| C(13)–C(14) | 1·472 (2) | 1·474 (2) | C(10)–C(11)–C(12) | 119·6 (2) | 119·2 (2) |
| | | | C(11)–C(12)–C(13) | 121·4 (1) | 122·3 (2) |
| | | | C(8)–C(13)–C(12) | 118·9 (1) | 118·6 (1) |
| | | | C(8)–C(13)–C(14) | 123·1 (1) | 124·0 (1) |
| | | | C(12)–C(13)–C(14) | 117·9 (1) | 117·4 (1) |
| | | | O(3)–C(14)–O(4) | 121·1 (1) | 121·9 (1) |
| | | | O(3)–C(14)–C(13) | 122·9 (1) | 123·6 (1) |
| | | | O(4)–C(14)–C(13) | 116·0 (1) | 114·5 (1) |

**Discussion.** The fractional coordinates of the two different molecules of diphenic acid (*A* and *B*) in the unit cell are given in Table 1.* Fig. 1 contains perspective drawings showing the atom labels and selected torsion angles. Distances and angles are presented in Table 2. A packing diagram is shown in Fig. 2. The molecules form hydrogen-bonded chains in the **b** direction through carboxylic acid dimers, with layers of chains stacking along the **c** direction. Two such layers of chains form because molecule *A* only hydrogen bonds to other molecules of *A*, and *B* only hydrogen bonds to other *B*'s.

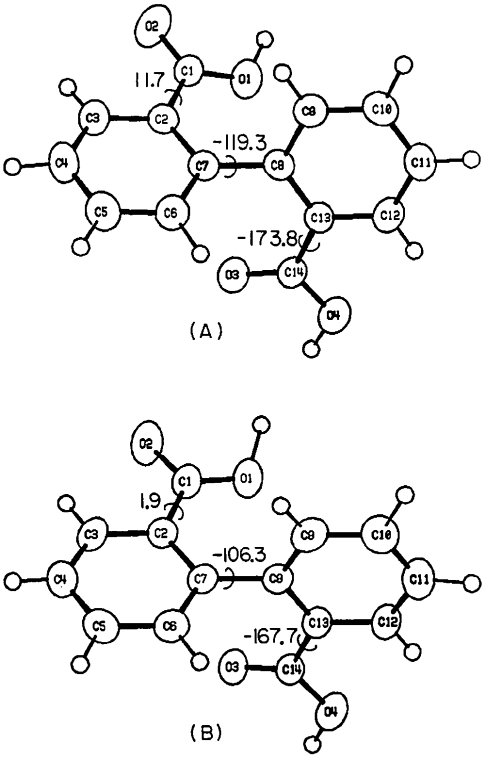

Fig. 1. *ORTEP* (Johnson, 1965) drawings of the two independent molecules of diphenic acid showing atom labels and selected torsion angles: O(2)–C(1)–C(2)–C(3), O(3)–C(14)–C(13)–C(12), C(2)–C(7)–C(8)–C(13). E.s.d.'s are 0·2–0·3°.

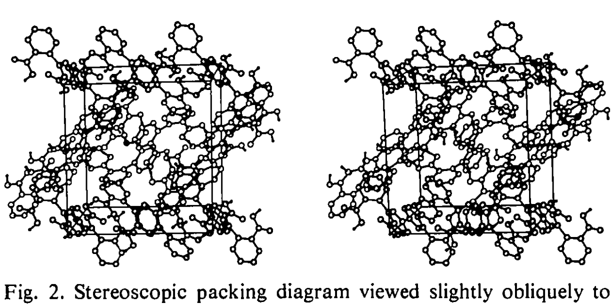

Fig. 2. Stereoscopic packing diagram viewed slightly obliquely to the *b* axis of the unit cell, with *c* horizontal.

A comparison of molecules *A* and *B* reveals that the largest difference in distance is 0·013 (3) Å, C(11)–C(12) and C(9)–C(10). The largest difference in bond angle is 1·6 (2)°, O(1)–C(1)–C(2). The clearest difference is in the torsion angles. The C(2)–C(7)–C(8)–C(13) [C(2)–C(1)–C(1′)–C(2′)] torsion angle differs by 13·0°. Both molecules have hydroxy group O(1) *syn* to the central bond, and hydroxy group O(4) *anti* to it. In molecule *B*, the carboxyl containing O(2) is nearly co-planar with its ring while in *A* it is 11·7° out of plane. The carboxyl with O(3) is 6·2° out of plane with its ring in molecule *A*, while in *B* it is 12·3° out of plane. The dihedral angle between the best planes of the rings is 71·3° in *A* and 83·6° in *B*. In the acid dimer structures of the two chains, all intermolecular hydrogen bonds are nearly linear, with angles at the H atom ranging from 168 (2) to 172 (2)°. O···O distances in the *A* chain are O(1*A*)···O(3*A*) 2·655 (1) and O(2*A*)···O(4*A*) 2·612 (1) Å. Similar distances in the *B* chain are O(1*B*)···O(3*B*) 2·811 (1) and O(2*B*)···O(4*B*) 2·553 (1) Å.

The chemical and physical reasons for the differences in the *A* and *B* molecules are not completely obvious. There is a trend between the carboxyl–ring-plane torsion angles and the O···O distances (O—H donor, out-of-plane angle, O···O distance): O(4*B*), 12·3°, 2·553 (1) Å; O(1*A*), 11·7°, 2·655 (1) Å; O(4*A*), 6·2°, 2·612 (1) Å; O(1*B*), 1·9°, 2·811 (1) Å. The more the carboxyl group is rotated out of the plane, the shorter is the O···O distance. This is consistent with the increased acid strength for carboxylic acids as a function of out-of-plane angle (Charton, 1971). A more acidic donor produces a shorter hydrogen bond. In molecule *B*, one carboxyl is nearly in the plane while the other is out of the plane, which results in a large difference in the two O···O distances. In molecule *A*, both carboxyls are rotated out of the plane and the two O···O distances are similar.

The structure of diphenic acid is different from other 2,2′-substituted biphenyls. The most significant difference is the disposition of the substituents in an *anti* conformation, |C(2)–C(1)–C(1′)–C(2′)| > 90°. Surveys of the conformations of 2,2′-substituted biphenyls (Rømming, Seip & Øymo, 1974; Ottersen, 1977; Leser & Rabinovich, 1978) indicate that only the *syn* conformation, |C(2)–C(1)–C(1′)–C(2′)| < 90°, has been observed in the crystalline state. Dihedral angles between the ring planes in diphenic acid are, however, quite similar to the others: 2,2′-dichloro- 69·2° (Rømming, Seip & Øymo, 1974), 2,2′-diamino- 58·2° (Ottersen, 1977), 2,2′-bis(chloroformyl)- 83·1° (Leser

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* Tables of H-atom coordinates, distances and angles involving H atoms, anisotropic thermal parameters and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43947 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& Rabinovich, 1978). These structures are symmetrically disposed about a crystallographic twofold axis, which is not the case for diphenic acid. The structure of biphenyl-2,2′-dicarbonyl dichloride (diphenic acid chloride) has both carbonyl O atoms directed toward the bond connecting the two rings (Leser & Rabinovich, 1978), whereas in diphenic acid only the O(3) carbonyl atom is located in this position. The differences in the structure of diphenic acid as compared to the other 2,2′-disubstituted biphenyls probably arise from intermolecular hydrogen bonding in the former.

The minimum-energy structure of diphenic acid calculated by extended Hückel theory methods as an isolated molecule (Botrel & Guerillot, 1974) has a dihedral angle of 85° with the acid groups *anti*, in agreement with the crystal structure. However, the calculated structure has the carboxyl groups orthogonal to the rings.

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# Incipient Type II β-Turn, Internal Water Bridge and Head-to-Tail Sequence in the Structure of Tri-α-aminoisobutyric Acid Dihydrate

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**Abstract.** $C_{12}H_{23}N_3O_4.2H_2O$, $M_r = 309$, monoclinic, $P2_1$, $a = 8{\cdot}504\ (2)$, $b = 11{\cdot}287\ (2)$, $c = 8{\cdot}922\ (2)$ Å, $\beta = 108{\cdot}65\ (1)°$, $V = 811{\cdot}4\ (4)$ Å$^3$, $Z = 2$, $D_x = 1{\cdot}27\ (2)$, $D_m = 1{\cdot}26$ Mg m$^{-3}$, $\lambda$(Cu $K\alpha$) $= 1{\cdot}5418$ Å, $\mu = 8{\cdot}53$ cm$^{-1}$, $F(000) = 336$, $T = 293$ K, final $R = 0{\cdot}040$ for 1499 observed reflections. The bond angles in the central residue exhibit conformation-dependent asymmetry about $C^{\alpha}$. The conformation of the molecule corresponds to an incipient type II′ (or type II) β-turn. The structure contains an internal water bridge, involving two water molecules, which connects the terminal amino group and the carbonyl group of the second residue. An interesting feature of the crystal is a zigzag head-to-tail sequence centred around a $2_1$ screw axis.

**Introduction.** We have earlier shown that the most prominent feature of molecular aggregation in the crystals of unprotected peptides containing residues of common naturally occurring amino acids is the 'head-to-tail' sequence in which the terminal amino and carboxylate groups are brought into periodic proximity (Suresh & Vijayan, 1985*a*,*b*). Such sequences, which occur ubiquitously in amino acid crystal structures as

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