(2) to be 1·529 (6) Å. There are a number of valence angles which differ significantly between structures (1) and (2), and in general, these differences are reflected in the calculated values. This implies the differences are real and reflect adjustments to ring strain and to intramolecular contacts induced by the different ring fusions. The torsion angles show the greatest discrepancies, and a twist-boat conformation is observed for the seven-membered ring in (1) and an almost ideal chair form for (2). The calculated and observed values show reasonable agreement; however, torsion angles more readily reflect the influence of intermolecular interactions which are neglected in the calcultions. The lactone ring in (1) is calculated to be more planar than observed and the cyclopentenone ring, although almost planar, with a different puckering pattern than observed. These small deviations from planarity again may reflect the influence of intermolecular interactions; however, there are only four intermolecular contacts, 2·38–2·44 Å, less than 3·00 Å.

We thank the National Science Foundation [INT-8214877 (WHW); BSR-8402017 (TJM)] and The Robert A. Welch Foundation [P-073 (WHW); F-130 (TJM)] for their financial support.

### References

ALLINGER, N. L. & YUH, Y. H. (1980). *Molecular Mechanics, MM2. Quantum Chem. Program Exch.* No. 395.

ALVARADO, S., CICCIO, J. F., CALZADA, J., ZABEL, V. & WATSON, W. H. (1979). *Phytochemistry*, **18**, 330.

CASTRO, V., CICCIO, J. F., ALVARADO, S., BOHLMANN, F., SCHMEDA-HIRSCHMANN, G. & JAKUPOVIC, J. (1983). *Justus Liebigs Ann. Chem.* pp. 974–981.

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

JOHNSON, C. K. (1971). *ORTEP*II. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee.

KING, R. M. & ROBINSON, H. (1969). *Brittonia*, **21**, 275–284.

LUENGO, D. H. DE, MISKI, M., GAGE, D. A., MABRY, T. J., KASHYAP, R. P. & WATSON, W. H. (1985). *Phytochemistry*. In the press.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

RYCHLEWSKA, V. (1981). *Pol. J. Chem.* **55**, 1895–1901.

STEWART, J. M., MACHIN, P. A., DICKINSON, C. W., AMMON, H. L., HECK, H. & FLACK, H. (1976). The *XRAY76* 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.

Syntex (1976). *XTL/XTLE Structure Determination System.* Syntex Analytical Instruments, Cupertino, California.

---

*Acta Cryst.* (1985). C**41**, 1128–1130

# Structure of *cis-transoid-cis*-6,11-Dioxatricyclo[7.3.0.0$^{4,8}$]-dodec-2-en-5,5,7,7,10,10,12,12-octacarbonitrile, $C_{18}H_6N_8O_2$

BY A. RODRIGUEZ-ROLDAN, A. MONGE* AND E. GUTIÉRREZ-PUEBLA

*Instituto de Química Inorgánica Elhuyar, Serrano* 113, *Madrid*-6, *Spain*

(*Received* 30 *July* 1984; *accepted* 7 *November* 1984)

**Abstract.** $M_r = 366·3$, monoclinic, $P2_1/c$, $a = 6·771$ (2), $b = 16·149$ (7), $c = 16·407$ (9) Å, $\beta = 100·08$ (5)°, $V = 1766$ (1) Å$^3$, $Z = 4$, $D_x = 1·377$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·09$ mm$^{-1}$, $F(000) = 744$, $T = 295$ K, $R = 0·050$ for 824 observed reflexions. The structure determination shows that in the adduct formed from one molecule of benzene and two molecules of tetracyanoethylene oxide, the benzene ring has lost its aromatic character. Bond lengths and angles are normal.

**Introduction.** The reaction of benzene and tetracyanoethylene oxide (TCNEO) (Linn & Benson, 1965) gives two different cycloadducts, one of them a monoadduct and the other a bisadduct.

This bisadduct is formed by reaction of one benzene molecule and two of TCNEO. This result suggests olefinic, not aromatic, behaviour of benzene. The structure of the bisadduct was difficult to resolve by spectroscopic techniques (Brown & Cookson, 1968; Diez-Barra, Pardo, Arriau, Elguero & Fruchier, 1984). However, theoretical methods and simulations of $^1$H NMR spectra have allowed us to exclude the structures formed by [$\pi^4 + \pi^4$] cycloaddition between the monoadduct and TCNEO; these methods, in fact, support the structure arising from [$\pi^4 + \pi^2$] cycloaddition.

---

* Author for correspondence. Departamento de Química Inorgánica, Facultad de Químicas, Universidad Complutense, Madrid-3, Spain.

**Experimental.** Clear, colourless, prismatic crystal, 0·3 × 0·4 × 0·4 mm, prepared by Diez-Barra *et al.* (1984). Nonius CAD-4*F* automatic diffractometer, cell dimensions refined by least-squares fitting of $\theta$ values of 25 reflexions; intensities of 3064 unique reflexions within $2 < \theta < 25°$, $h,k,l$ range from 0,0,−19 to 8,19,19, monochromatic Mo $K\alpha$ radiation, $\omega/2\theta$ scans. Three reflexions monitored periodically during data collection showed no crystal decomposition; intensities corrected for Lorentz and polarization effects; 824 considered observed $[I > 2\sigma(I)]$; no absorption correction. Scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974). Structure solved by direct methods with *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977), best $E$ map revealed all non-H atoms; after anisotropic full-matrix least-squares refinement, with $\sum w(|F_o| - |F_c|)^2$ minimized, $R = 0{\cdot}07$; difference synthesis calculated with reflexions with $\sin\theta/\lambda < 0{\cdot}5$ Å$^{-1}$ showed all H atoms as the highest peaks of the map; final refinement with fixed isotropic temperature factors for H atoms and unit weights led to $R = 0{\cdot}050$. Max. and average shift/error in final LS cycle 0·48 and 0·07; final difference synthesis had no electron density $> 0{\cdot}20$ e Å$^{-3}$ and $< -0{\cdot}19$ e Å$^{-3}$. No correction for secondary extinction. Most of the calculations performed with *XRAY*70 (Stewart, Kundell & Baldwin, 1970). LS planes and torsion angles computed with *PARST*5 (Nardelli, Musatti, Domiano & Andreetti, 1965).

**Discussion.** Table 1 shows the final atomic parameters.* Fig. 1 shows the geometry of the structure and the atom labelling. Bond lengths and angles together with their e.s.d.'s are included in Table 2.

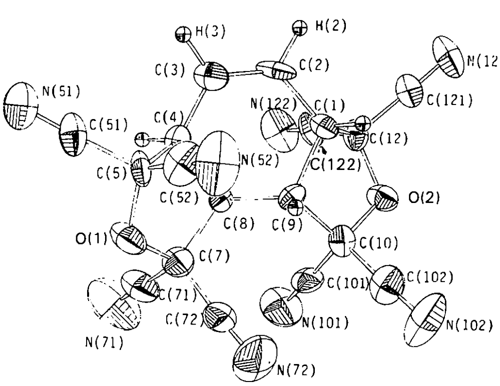

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule, showing the atom numbering.

Table 1. *Atomic coordinates and isotropic thermal parameters* (Å$^2$ × 10$^3$, × 10$^2$ *for* H)

For non-H atoms, $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j \cos(a_i, a_j)$. For H atoms, $T = \exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

| | $x$ | $y$ | $z$ | $U_{eq}/U$ |
|---|---|---|---|---|
| N(71) | 0·9162 (14) | −0·0754 (7) | 0·5550 (6) | 88 (4) |
| C(1) | 0·7427 (13) | 0·1400 (6) | 0·8332 (5) | 32 (4) |
| C(2) | 0·7614 (15) | 0·2204 (6) | 0·7942 (7) | 42 (4) |
| C(3) | 0·7573 (14) | 0·2276 (5) | 0·7140 (7) | 37 (4) |
| C(4) | 0·7565 (14) | 0·1577 (5) | 0·6539 (6) | 30 (3) |
| C(5) | 0·5496 (13) | 0·1470 (6) | 0·5896 (5) | 37 (3) |
| O(1) | 0·5644 (9) | 0·0656 (4) | 0·5570 (4) | 40 (2) |
| C(7) | 0·6639 (13) | 0·0125 (5) | 0·6217 (6) | 35 (3) |
| C(8) | 0·7700 (13) | 0·0700 (5) | 0·6959 (5) | 28 (3) |
| C(9) | 0·6804 (13) | 0·0650 (5) | 0·7746 (5) | 24 (3) |
| C(10) | 0·7543 (14) | −0·0109 (5) | 0·8342 (6) | 41 (4) |
| O(2) | 0·8918 (10) | 0·0220 (4) | 0·9048 (4) | 51 (3) |
| C(12) | 0·9320 (14) | 0·1063 (6) | 0·8925 (5) | 38 (4) |
| C(51) | 0·3675 (15) | 0·1550 (6) | 0·6250 (6) | 41 (4) |
| N(51) | 0·2236 (13) | 0·1536 (6) | 0·6513 (6) | 69 (4) |
| C(52) | 0·5407 (15) | 0·2052 (6) | 0·5195 (6) | 43 (4) |
| N(52) | 0·5264 (14) | 0·2500 (6) | 0·4670 (6) | 68 (4) |
| C(71) | 0·8101 (14) | −0·0374 (6) | 0·5855 (6) | 53 (4) |
| C(72) | 0·5135 (17) | −0·0433 (6) | 0·6472 (6) | 44 (4) |
| N(72) | 0·3940 (16) | −0·0838 (6) | 0·6678 (6) | 79 (5) |
| C(101) | 0·5861 (17) | −0·0478 (7) | 0·8685 (7) | 58 (5) |
| N(101) | 0·4626 (17) | −0·0768 (8) | 0·8935 (8) | 117 (6) |
| C(102) | 0·8573 (19) | −0·0749 (6) | 0·7932 (7) | 59 (5) |
| N(102) | 0·9339 (19) | −0·1209 (7) | 0·7582 (7) | 121 (7) |
| C(121) | 1·1190 (16) | 0·1137 (7) | 0·8580 (6) | 52 (4) |
| N(121) | 1·2613 (13) | 0·1150 (7) | 0·8329 (6) | 78 (5) |
| C(122) | 0·9651 (14) | 0·1471 (7) | 0·9745 (6) | 48 (4) |
| N(122) | 0·9921 (16) | 0·1810 (6) | 1·0362 (6) | 78 (5) |
| H(1) | 0·656 (14) | 0·141 (6) | 0·871 (6) | 3 (4) |
| H(2) | 0·793 (14) | 0·271 (6) | 0·831 (6) | 3 (5) |
| H(3) | 0·747 (14) | 0·280 (6) | 0·684 (6) | 3 (4) |
| H(4) | 0·855 (15) | 0·161 (6) | 0·621 (6) | 3 (4) |
| H(8) | 0·907 (14) | 0·059 (6) | 0·708 (6) | 3 (4) |
| H(9) | 0·532 (14) | 0·066 (5) | 0·762 (5) | 3 (4) |

Table 2. *Bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| C(1)–C(2) | 1·463 (14) | C(9)–C(10) | 1·593 (12) |
| C(1)–C(9) | 1·558 (12) | C(10)–O(2) | 1·454 (11) |
| C(1)–C(12) | 1·565 (12) | C(10)–C(101) | 1·481 (16) |
| C(2)–C(3) | 1·316 (16) | C(10)–C(102) | 1·474 (15) |
| C(3)–C(4) | 1·492 (13) | O(2)–C(12) | 1·410 (12) |
| C(4)–C(5) | 1·558 (12) | C(12)–C(121) | 1·479 (14) |
| C(4)–C(8) | 1·571 (12) | C(12)–C(122) | 1·480 (13) |
| C(5)–O(1) | 1·429 (11) | C(51)–N(51) | 1·133 (14) |
| C(5)–C(51) | 1·458 (14) | C(52)–N(52) | 1·116 (14) |
| C(5)–C(52) | 1·478 (14) | C(71)–N(71) | 1·127 (15) |
| O(1)–C(7) | 1·437 (10) | C(72)–N(72) | 1·136 (15) |
| C(7)–C(8) | 1·598 (12) | C(101)–N(101) | 1·099 (18) |
| C(7)–C(71) | 1·479 (14) | C(102)–N(102) | 1·120 (17) |
| C(7)–C(72) | 1·475 (14) | C(121)–N(121) | 1·112 (15) |
| C(8)–C(9) | 1·522 (13) | C(122)–N(122) | 1·137 (15) |
| | | | |
| C(9)–C(1)–C(12) | 102·5 (7) | C(1)–C(9)–C(8) | 112·2 (7) |
| C(2)–C(1)–C(12) | 117·2 (8) | C(8)–C(9)–C(10) | 115·6 (7) |
| C(2)–C(1)–C(9) | 117·1 (8) | C(1)–C(9)–C(10) | 101·4 (7) |
| C(1)–C(2)–C(3) | 121·8 (9) | C(9)–C(10)–C(102) | 112·5 (8) |
| C(2)–C(3)–C(4) | 125·7 (9) | C(9)–C(10)–C(101) | 111·3 (8) |
| C(3)–C(4)–C(8) | 113·7 (7) | C(9)–C(10)–O(2) | 107·3 (7) |
| C(3)–C(4)–C(5) | 117·9 (8) | C(101)–C(10)–C(102) | 110·4 (8) |
| C(5)–C(4)–C(8) | 101·9 (7) | O(2)–C(10)–C(102) | 109·4 (8) |
| C(4)–C(5)–C(52) | 111·7 (8) | O(2)–C(10)–C(101) | 105·8 (8) |
| C(4)–C(5)–C(51) | 113·8 (7) | C(10)–O(2)–C(12) | 110·6 (7) |
| C(4)–C(5)–O(1) | 104·3 (7) | C(1)–C(12)–O(2) | 105·5 (7) |
| C(51)–C(5)–C(52) | 109·4 (8) | C(1)–C(12)–C(121) | 113·4 (8) |
| O(1)–C(5)–C(52) | 106·8 (7) | O(2)–C(12)–C(122) | 107·6 (8) |
| O(1)–C(5)–C(51) | 110·5 (8) | O(2)–C(12)–C(121) | 109·4 (7) |
| C(5)–O(1)–C(7) | 109·1 (6) | C(1)–C(12)–C(122) | 112·8 (8) |
| O(1)–C(7)–C(72) | 108·5 (8) | C(121)–C(12)–C(122) | 108·0 (8) |
| O(1)–C(7)–C(71) | 106·8 (7) | C(5)–C(51)–N(51) | 173·7 (11) |
| O(1)–C(7)–C(8) | 107·8 (7) | C(5)–C(52)–N(52) | 177·2 (11) |
| C(71)–C(7)–C(72) | 109·0 (8) | C(7)–C(71)–N(71) | 177·2 (11) |
| C(8)–C(7)–C(72) | 112·3 (8) | C(7)–C(72)–N(2) | 177·5 (11) |
| C(8)–C(7)–C(71) | 112·3 (8) | C(10)–C(101)–N(101) | 178·5 (12) |
| C(4)–C(8)–C(7) | 101·1 (7) | C(10)–C(102)–N(102) | 176·2 (12) |
| C(7)–C(8)–C(9) | 115·0 (7) | C(12)–C(121)–N(121) | 176·4 (12) |
| C(4)–C(8)–C(9) | 113·3 (7) | C(12)–C(122)–N(122) | 177·6 (12) |

---

* Lists of structure factors, anisotropic temperature factors, bond distances and angles for the H atoms, least-squares-planes' calculations and selected torsion angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42074 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The six-membered ring is not planar, the average and maximum deviations from the least-squares plane being 0·138 and 0·243 (9) Å respectively.

The magnitudes of the bond lengths and angles are also consistent with loss of aromatic character in this ring.

### References

BROWN, P. & COOKSON, R. C. (1968). *Tetrahedron*, **24**, 2551–2566.

DIEZ-BARRA, E., PARDO, C., ARRIAU, J., ELGUERO, J. & FRUCHIER, A. (1984). *An. Quím.* Submitted for publication.

*International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

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

LINN, W. J. & BENSON, R. E. (1965). *J. Am. Chem. Soc.* **87**, 3657–3665.

MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *MULTAN77. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

NARDELLI, M., MUSATTI, A., DOMIANO, P. & ANDREETTI, G. D. (1965). *Ric. Sci.* **35**, 807–810.

STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The *XRAY70* system. Computer Science Center, Univ. of Maryland, College Park, Maryland.

---

*Acta Cryst.* (1985). C**41**, 1130–1133

# Methyl 3,5-Di-*tert*-butyl-4-diisopropylamino-1$H^+$-pyridazinium-6-phosphonate Dichloromethane Solvate, $C_{19}H_{36}N_3O_3P.0{\cdot}85\ CH_2Cl_2$: a Betaine Having a Nonplanar Pyridazinium Ring

BY GERHARD MAAS

*Fachbereich Chemie der Universität Kaiserslautern, Postfach* 3049, *D*-6750 *Kaiserslautern, Federal Republic of Germany*

(*Received* 8 *October* 1984; *accepted* 14 *March* 1985)

**Abstract.** $M_r = 457{\cdot}69$, monoclinic, $P2_1/n$, $a = 12{\cdot}491\ (4)$, $b = 17{\cdot}206\ (7)$, $c = 12{\cdot}532\ (5)$ Å, $\beta = 111{\cdot}27\ (3)^\circ$, $V = 2510\ (1)$ Å$^3$, $Z = 4$, $D_x = 1{\cdot}21$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 3{\cdot}16$ cm$^{-1}$, $F(000) = 982{\cdot}8$, $T = 297$ K, $R = 0{\cdot}073$ for 3368 observed reflections. The molecule exists as a betaine, in which the acidic proton of the phosphonic acid group has been transferred to a nitrogen atom of the pyridazine ring. This ring is no longer planar but assumes a boat conformation; the bond pattern is best described as a 4-iminio-substituted 1,4-dihydropyridazine. In the crystal, the betaine forms a dimer held together by two N—H···O hydrogen bonds.

**Introduction.** The structure analysis was originally undertaken in order to confirm the substitution pattern of the heterocyclic ring. Inspection of molecular structure, then, revealed three noticeable features: (i) The molecule exists as a betaine, *i.e.* a proton transfer from the phosphonic acid function to a ring nitrogen has taken place. This was not unexpected, as 4-aminopyridazines are more basic than pyridines by more than one p$K_a$ unit (Lenhert & Castle, 1973), and compounds like nicotinic acid (Gupta & Kumar, 1975) or pyridine-3-sulfonic acid (Chandrasekhar, 1977) crystallize in the betaine form as well. (ii) The pyridazinium ring is not planar, but assumes a distinct boat form. (iii) The betaine forms a dimer by means of two P=O···H—N hydrogen bonds, a situation reminiscent of α-amino acids (Koetzle & Lehmann, 1976, and references cited therein) although, in the latter, such a dimer is only a building block in a three-dimensional network.

**Experimental.** The yellow crystals were a gift from M. Regitz and K. Feith; their preparation will be given elsewhere (Feith, 1985). Suitable crystals were obtained by crystallization from dichloromethane, but not all of the solvent could be removed without destroying the crystals. From an elemental analysis and the $^1$H NMR spectrum, a $CH_2Cl_2$ content of 0·85 mol per mol of pyridazine was calculated. Crystal size 0·5 × 0·3 × 0·5 mm, Enraf–Nonius CAD-4 diffractometer, monochromatized Mo $K\alpha$ radiation. Cell constants from least-squares refinement of $\theta$ values of 23 reflections with $20{\cdot}20 \leq 2\theta \leq 23{\cdot}10^\circ$. No absorption correction. Data collection: $\theta$ range 2·0 to 25·0°, $\theta/2\theta$ scan, scan width $(0{\cdot}95 + 0{\cdot}35\tan\theta)^\circ$, scan speed 1·42 to

0108-2701/85/071130-04$01.50