between the TNB's and the phenyl rings of the stilbene. In the dibenz[*a,h*]anthracene.TNB$_2$ complex the TNB molecules are also situated over the rings at the extremities of the donor molecule, and the center of the molecule is essentially uncomplexed in this structure as well (Zacharias, 1976). The distance of the TNB atoms from the 'best plane' of the S molecule varies from 3·11 Å for O(4TN) to 3·77 Å for O(2TN); the distances of the C atoms in the TNB ring are in the range 3·31 Å for C(3TN) to 3·48 Å for C(6TN). Closest interplanar atom···atom contacts are all quite normal, the shortest being C(5ST)···N(3TN) of 3·34 Å.

We wish to thank Dr Zippora Shakked of the Weizmann Institute of Science for providing the search of the Cambridge Crystallographic Data File, and the staff of the Computing Center of the Ben-Gurion University of the Negev for assistance. One of us (JB) wishes to acknowledge the warm hospitality of Professor I. C. Paul of the University of Illinois, where this manuscript was prepared. Thanks are also due to Dr D. Zacharias of the Institute for Cancer Research for providing us with coordinates of the dibenz[*a,h*]-anthracene. TNB structure prior to publication.

References

Bar, I., Bernstein, J. & Christensen, A. (1976). *Acta Cryst.* B**32**, 1609–1611.

Bernstein, J. (1975). *Acta Cryst.* B**31**, 1268–1271.

Bernstein, J. & Mirsky, K. (1978). *Acta Cryst.* A**34**, 161–165.

Brown, C. J. (1966*a*). *Acta Cryst.* **21**, 146–152.

Brown, C. J. (1966*b*). *Acta Cryst.* **21**, 153–158.

Choi, C. S. & Abel, J. E. (1972). *Acta Cryst.* B**28**, 193–201.

Domenicano, A., Vaciago, A. & Coulson, C. A. (1975). *Acta Cryst.* B**31**, 221–234.

Finder, C. J., Newton, M. G. & Allinger, N. L. (1974). *Acta Cryst.* B**30**, 411–415.

Frank, G. W., Myasnikova, R. M. & Kitaigorodskii, A. I. (1971). *Sov. Phys. Crystallogr.* **16**, 270–274.

Hertel, E. & Schneider, K. (1932). *Z. Phys. Chem. (Leipzig)*, **15**, 79–83.

Hoekstra, A., Meertens, P. & Vos, A. (1975). *Acta Cryst.* B**31**, 2813–2817.

Kodoma, T. & Kumakura, S. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1081–1084.

Robertson, J. M. & Woodward, I. (1937). *Proc. R. Soc. London Ser. A*, **162**, 568–583.

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

Sudborough, J. J. (1910). *J. Chem. Soc.* pp. 773–798.

Sudborough, J. J. (1916). *J. Chem. Soc.* pp. 1339–1348.

Trætteberg, J. M., Frantsen, E. B., Mijlhoff, F. C. & Hoekstra, A. (1975). *J. Mol. Struct.* **26**, 57–68.

Walczak, M. & Stucky, G. (1976). *J. Am. Chem. Soc.* **98**, 5531–5539.

Zacharias, D. E. (1976). Am. Crystallogr. Assoc. Winter Meet., Clemson, South Carolina, p. 12.

Acta Cryst. (1978). B**34**, 3441–3444

(2*S*,3*R*,3a*S*,5*S*)-3a-Allyl-5-methoxy-3-methyl-2-(3′,4′-dimethoxyphenyl)-6-oxo-2,3,3a,4,5,6-hexahydrobenzofuran (a Neolignan: Porosin)

By Koychi Tomita

Instituto de Química de Araraquara, CP 174, Araraquara, São Paulo, Brazil

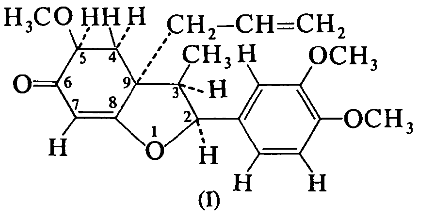
and Robert D. Rosenstein and Regina H. Almeida Santos

Instituto de Física e Química de São Carlos, São Paulo, Brazil

(*Received* 7 *November* 1977; *accepted* 3 *July* 1978)

Abstract. $C_{21}H_{26}O_5$, orthorhombic, $P2_12_12$, a = 23·727 (5), b = 9·736 (5), c = 8·318 (5) Å, V = 1921·5 Å^3, Z = 4, D_c = 1·24 g cm^{-3}. The structure was solved by the direct method and Fourier difference syntheses and refined by the full-matrix least-squares method to an R value of 0·095 for 1584 observed structure amplitudes measured with Mo $K\alpha$ radiation on an automatic diffractometer.

Introduction. Porosin (I), a neolignan, was isolated from the trunk of the *Ocotea porosa* tree as part of a series of studies of natural products (Aiba, Braz Filho & Gottlieb, 1973). Two related phenyl-benzofuran neolignans have been studied by structure analysis by Tomita, Rosenstein & Jeffrey (1977) and by Tomita, Jeffrey & Shiono (1977).



(I)

A slightly yellow crystal of (I) showed the systematic absences on Weissenberg photographs ($h00$ for h odd and $0k0$ for k odd) of the space group $P2_12_12$. The unit-cell dimensions and three-dimensional intensity data were measured on a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation, using a crystal of dimensions 0·8 × 0·5 × 0·4 mm. Of the 1975 independent reflections measured, 1584 had intensities greater than $2\sigma(I)$. The unobserved reflections were given values of $0{\cdot}5\sigma(I)$, where $\sigma(I)$ is from counting statistics. No corrections were made for absorption or extinction.

The application of the program *MULTAN* (Germain, Main & Woolfson, 1971) gave an E map which showed 20 of the 26 C and O atoms. The six remaining atoms were located on a difference synthesis map. Isotropic followed by anisotropic refinement resulted in an R factor of 0·11. At this stage, a difference map showed the positions of 12 H atoms; the remaining 14 were given positions consistent with C—H bonds of 1·0 Å and tetrahedral or trigonal C geometry. Final refinement gave an R value of 0·095 for 1584 observed data, using unit weights. The H atoms were given isotropic temperature factors equivalent to the anisotropic factors of the atoms to which they were attached. The H positional and thermal parameters were not refined. The scattering factors used were those of Cromer & Waber (1965). The final positional parameters, with their estimated standard deviations, are listed in Table 1.*

All calculations were carried out on the Instituto de Física e Quimica de São Carlos PDP-11/45 computer, using SDP programs.

Discussion. The atomic numbering and the bond lengths are given in Fig. 1. The conformation of the molecule is given in Fig. 2 and Table 2. The molecular packing is shown in Fig. 3. The torsion angles and bond lengths are consistent with the molecular configuration shown in (I). The 2*S*,3*R*,3a*S*,5*S* absolute configuration is based on the chemical studies of Aiba, Braz Filho & Gottlieb (1973) and Aiba, Gottlieb, Yoshida, Mourão & Gottlieb (1976) of this and related compounds. The only abnormal length is the C(13)—C(14) bond distance, which is 1·236 (17) Å. This bond is shortened as a result of the large thermal motion of the terminal allyl atom C(14). The same shortening of this bond was observed in the structure of related molecules, (2*S*,3*S*,3a*S*)-5-allyl-3a-methoxy-2-(3′,4′,5′-trimethoxyphenyl)-3-methyl-6-oxo-2,3,3a,6-tetrahydrobenzofuran (Tomita, Rosenstein & Jeffrey, 1977) and (2*S*,3*S*,5*R*)-5-allyl-5-methoxy-2-(3′,4′,5′-trimethoxyphenyl)-3-methyl-6-oxo-2,3,5,6-tetrahydrobenzofuran (Tomita, Jeffrey & Shiono, 1977).

In the original structure proposed for porosin by Aiba, Braz Filho & Gottlieb (1973) the dihydrobenzofuran ring was different as shown in (II), but later the chemical and NMR results were interpreted in terms of

Table 1. *Atomic parameters for porosin*

Atomic coordinates (× 10^4) for non-hydrogen atoms and (× 10^3) for hydrogen atoms. Estimated standard deviations are given in parentheses.

	x	y	z
O(1)	4062 (3)	7402 (6)	−1538 (8)
O(2)	5242 (3)	7402 (9)	−7152 (8)
O(3)	5645 (3)	8664 (7)	−4545 (10)
O(4)	2082 (3)	4904 (8)	1754 (9)
O(5)	2779 (2)	3267 (7)	3159 (9)
C(2)	3525 (3)	6694 (9)	−1919 (10)
C(3)	3626 (4)	6028 (9)	−3571 (10)
C(4)	4415 (4)	6705 (10)	−5696 (10)
C(5)	4847 (4)	7825 (10)	−6002 (10)
C(6)	5153 (4)	8247 (9)	−4459 (10)
C(7)	4870 (4)	8138 (10)	−2993 (10)
C(8)	4340 (4)	7608 (9)	−2931 (10)
C(9)	4001 (3)	7155 (9)	−4359 (10)
C(10)	3909 (5)	4644 (9)	−3467 (10)
C(11)	5139 (6)	7769 (20)	−8660 (20)
C(12)	3631 (4)	8394 (9)	−4984 (10)
C(13)	3348 (4)	8115 (11)	−6517 (10)
C(14)	2861 (8)	8442 (20)	−6884 (30)
C(15)	3365 (4)	5822 (9)	−502 (10)
C(16)	2800 (3)	5788 (9)	−58 (10)
C(17)	2627 (4)	4955 (10)	1192 (10)
C(18)	3002 (4)	4080 (9)	1956 (10)
C(19)	3561 (4)	4149 (9)	1547 (10)
C(20)	3738 (3)	5008 (10)	298 (10)
C(21)	1675 (4)	5818 (13)	1155 (20)
C(22)	3124 (5)	2219 (10)	3781 (10)
H1(C2)	318	731	−207
H1(C3)	327	577	−417
H1(C4)	464	587	−532
H2(C4)	423	644	−669
H1(C5)	463	864	−642
H1(C7)	506	846	−198
H1(C10)	371	399	−273
H2(C10)	430	475	−300
H3(C10)	395	420	−451
H1(C11)	529	723	−958
H2(C11)	528	874	−878
H3(C11)	472	783	−881
H1(C12)	333	858	−418
H2(C12)	387	923	−507
H1(C13)	359	772	−742
H1(C14)	272	821	−793
H2(C14)	264	883	−604
H1(C16)	252	636	−62
H1(C19)	384	358	220
H1(C20)	415	503	−3
H1(C21)	188	650	37
H2(C21)	154	646	209
H3(C21)	136	543	68
H1(C22)	312	139	302
H2(C22)	298	186	481
H3(C22)	351	250	391

---

* Lists of structure factors, anisotropic thermal parameters and bond angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33732 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

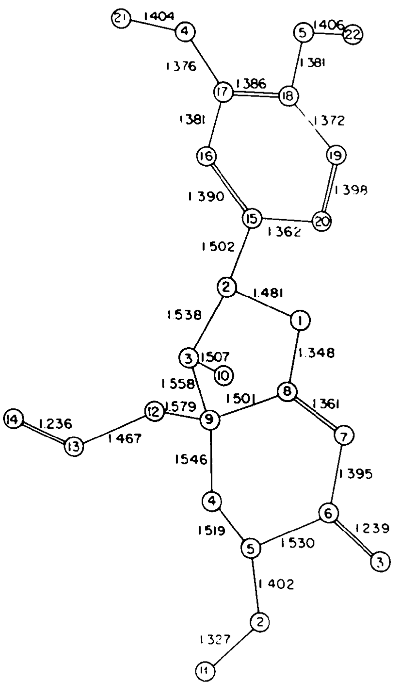


Fig. 1. Atomic numbering and bond distances (Å). The standard deviations are below 0·012 Å, except for C(13)–C(14), where it is 0·017 Å.

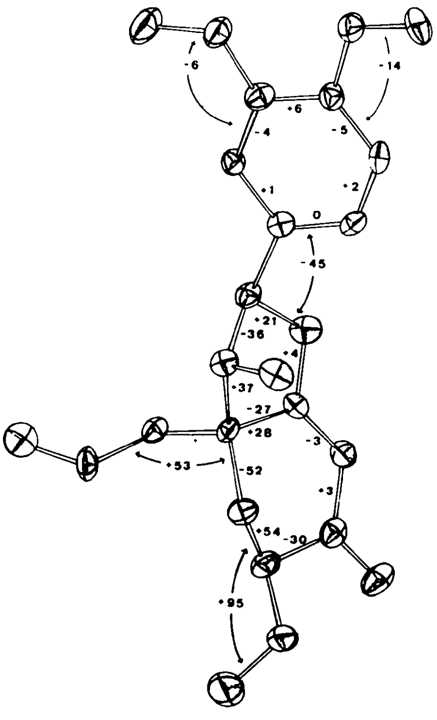


Fig. 2. Torsion angles in degrees and thermal ellipsoids at 50% probability (Johnson, 1965). Except where indicated by arrows, the torsion angles refer to the ring bonds.

Table 2. *Torsion angles defining the configuration at the asymmetric centers* (°)

C(8)–O(1)–C(2)–C(15)	+150
C(9)–C(3)–C(2)–C(15)	−158
C(10)–C(3)–C(2)–C(15)	−37
O(1)–C(2)–C(3)–C(10)	+85
C(8)–C(9)–C(3)–C(10)	−84
O(3)–C(6)–C(5)–O(2)	+27
C(7)–C(6)–C(5)–O(2)	−153
C(9)–C(4)–C(5)–O(2)	+177
O(1)–C(8)–C(9)–C(12)	+90
C(2)–C(3)–C(9)–C(12)	−79
C(5)–C(4)–C(9)–C(12)	+67
C(10)–C(3)–C(9)–C(12)	+160

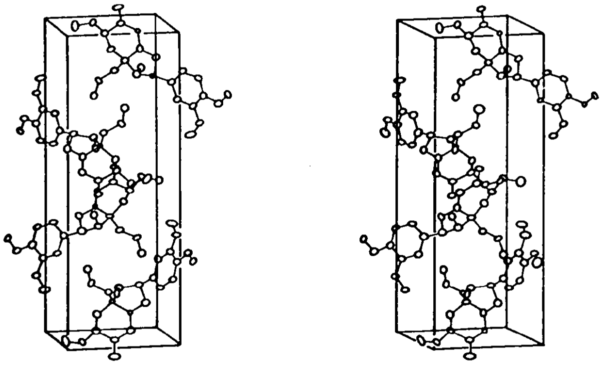
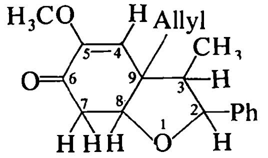


Fig. 3. Unit-cell contents and molecular packing. The *c* axis is horizontal, and the *a* axis is vertical.

(I), in agreement with the X-ray results (Aiba, Gottlieb, Yoshida, Mourão & Gottlieb, 1976).



(II)

In (I), the dihydrobenzo ring has the sofa conformation with C(4) out of the plane of the other five atoms. The furan ring is close to an envelope conformation with C(3) out of the plane. The displacements of C(4) and C(3) out of the mean ring planes are both *endo* relative to C(15). The phenyl ring is inclined at 45° to the furan ring. It has minor distortions with displacements of ±0·03 Å from the mean plane of the ring.

The molecular packing is due to van der Waals forces. The shortest intermolecular contacts involving non-hydrogen atoms are 3·347 Å for C(22)···O(3) $(1-x, 1-y, 1+z)$, 3·392 Å for C(19)···O(2) $(1-x, 1-y, 1+z)$, 3·444 Å for C(2)···O(4) $(\frac{1}{2}-x, \frac{1}{2}+y, -z)$, 3·455 Å for C(14)···O(5) $(\frac{1}{2}-x, \frac{1}{2}+y, -z)$ and 3·499 Å for C(12)···O(4) $(\frac{1}{2}-x, \frac{1}{2}+y, -z)$.

This work was supported by the Fundação de Amparo a Pesquisa do Estado de São Paulo (FAPESP), Conselho Nacional de Desenvolvimento Cientifico e Tecnológico (CNPq) and Financiadora de Estudos e Projetos (FINEP). We thank Professor O. R. Gottlieb and Professor Y. P. Mascarenhas of the Universidade de São Paulo, Brazil, for supplying the crystals and for valuable suggestions and encouragement.

References

Aiba, C. J., Braz Filho, R. & Gottlieb, O. R. (1973). *Phytochemistry*, **12**, 413–416.

Aiba, C. J., Gottlieb, O. R., Yoshida, M., Mourão, J. C. & Gottlieb, H. E. (1976). *Phytochemistry*, **15**, 1031–1032.

Cromer, D. T. & Waber, J. T. (1965). *Acta Cryst.* **18**, 104–109.

Germain, G., Main, P. & Woolfson, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

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

Tomita, K., Jeffrey, G. A. & Shiono, R. (1977). *Acta Cryst.* B**33**, 3576–3580.

Tomita, K., Rosenstein, R. D. & Jeffrey, G. A. (1977). *Acta Cryst.* B**33**, 2678–2680.

Acta Cryst. (1978). B**34**, 3444–3446

3-Amino-4-methylfurazan

By D. Viterbo

Istituto di Chimica Fisica dell'Universitá, Corso M. D'Azeglio 48, 10125 *Torino, Italy*

and A. Serafino

Istituto di Chimica Farmaceutica e Tossicologica dell'Universitá, Corso Raffaello 31, 10125 *Torino, Italy*

(*Received* 5 *June* 1978; *accepted* 4 *July* 1978)

Abstract. $C_3H_5N_3O$, monoclinic, $P2_1/c$, $a = 10{\cdot}968\,(2)$, $b = 10{\cdot}648\,(2)$, $c = 8{\cdot}216\,(1)$ Å, $\beta = 92{\cdot}72\,(1)°$; $Z = 8$, $D_c = 1{\cdot}37$ g cm^{-3}; m.p. 72–73°C. The compound was prepared [Cusmano & Tiberio (1951). *Gazz. Chim. Ital.* **81**, 106–116] and crystallized from water as prismatic crystals. The two independent molecules do not show significant geometrical differences. The five-membered rings are asymmetrical as a consequence of a significant difference between the two N—O bonds.

Introduction. The present structural analysis was undertaken as part of an extensive study of the structural properties of disubstituted furoxans and furazans. In particular, after analyzing several compounds with electron-withdrawing substituents, we are now turning our attention to some electron-donor substituents such as the NH_2 group.

The cell parameters were determined and refined from diffractometer data. The systematic absence of reflexions $0k0$ with k odd and $h0l$ with l odd uniquely indicated the space group $P2_1/c$, with two independent molecules in the asymmetric part of the unit cell. The intensities of 1418 independent reflexions were measured at room temperature, on a Philips PW 1100 four-circle diffractometer (graphite-monochromatized Cu $K\alpha$ radiation) using the θ–2θ scanning technique; 423 reflexions with $I \leq 2\sigma(I)$ were considered as unobserved and not used for the refinement.

The solution was found using the program *MULTAN* (Declercq, Hull, Germain, Lessinger, Main & Woolfson, 1976); with 200 E's ($E_{\min} = 1{\cdot}47$) and 2000 $\sum_2$ relationships, 16 sets of phases were generated.

The E map computed with the set having the best figures of merit revealed all 14 non-hydrogen atoms, whose positions and individual isotropic temperature factors were initially refined by three full-matrix least-squares cycles. The H atoms were located on a difference map computed after three further anisotropic cycles. Attempts at isotropically refining the H atoms with no constraint caused them to drift from their stereochemically plausible positions. Using the *SHELX* system of programs (Sheldrick, 1976), the C—H, N—H and H—H distances were then constrained to their normal values; the final cycles with anisotropic temperature factors assigned to all non-hydrogen atoms converged to an R value of 0·053 (R value for all 1418 measured data: 0·078). The weighting scheme was $w = 1/[\sigma^2(F_o) + aF_o^2]$, where $\sigma(F_o)$ is the estimated standard deviation of the observed amplitudes as derived from counting statistics and a is a variable parameter to be adjusted after each cycle; its final value was $a = 0{\cdot}03$ and the final weighted R factor was 0·061. The atomic parameters for both molecules in the