$$\mathcal{R}^{+} = \tfrac{1}{8}(R_{\parallel} + R_{\perp}) - \tfrac{1}{4}Re(r_{\parallel}r_{\perp}) \qquad \text{(A.4)}$$

where $R_{\parallel}$ and $R_{\perp}$ equal $|r_{\parallel}|^2$ and $|r_{\perp}|^2$ and are the usual expressions for normal incidence reflectivity.[39] Similarly, with the second polarizer in the y direction (parallel), we find

$$\mathcal{R}^{\parallel} = \tfrac{3}{8}(R_{\parallel} + R_{\perp}) + \tfrac{1}{4}Re\,(r_{\parallel}r_{\perp}) \qquad \text{(A.5)}$$

Note that $\mathcal{R}^{+} + \mathcal{R}^{\parallel}$ gives $(R_{\parallel} + R_{\perp})/2$ as expected. Also, as expected, $\mathcal{R}^{+} + \mathcal{R}^{\parallel}$ gives 1 and ½ for the two limiting cases of perfect reflection in all directions ($r_{\parallel} = r_{\perp} = -1$) and perfect reflection in one dimension ($r_{\parallel} = -1$; $r_{\perp} = 0$). For the limiting case of an isotropic absorber with reflectivity R_{iso}, we find $\mathcal{R}^{+} = 0$ and $\mathcal{R}^{\parallel} = R_{\text{iso}}$, as required for the case of normal incidence collection.

Since $R_{\perp}$ is unstructured in the visible, $\mathcal{R}^{+}$ will more or less follow $R_{\parallel}$ as we observe in Figure 2. Also, since $r_{\perp}$ is real, $Re(r_{\parallel}r_{\perp})$ is always positive and the ratio $\mathcal{R}^{\parallel}/\mathcal{R}^{+}$ is always greater than 3. As stated earlier, we observe $\mathcal{R}^{\parallel}/\mathcal{R}^{+} \approx 5$. However, it is difficult to argue even qualitatively the effect on this ratio when all angles of incidence are included.

References and Notes

(1) G. Wegner, *Z. Naturforsch. B*, **24**, 824 (1969).
(2) G. Wegner, *Makromol. Chem.*, **145**, 85 (1971).
(3) R. H. Baughman, *J. Appl. Phys.*, **43**, 4362 (1972); *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1511 (1974).
(4) D. Bloor, L. Koski, and G. C. Stevens, *J. Mater. Sci.*, **10**, 1689 (1975).
(5) D. Kobelt and E. F. Paulus, *Acta Crystallogr., Sect. B*, **30**, 232 (1973).
(6) E. Hadicke, E. C. Mez, C. H. Krauch, G. Wegner, and J. Kaiser, *Angew. Chem.*, **83** 253 (1971).
(7) A. Enkelmann and J. B. Lando, preprint "Crystal and Molecular Structure of Poly(5,7-dodecadiyne-diol-1,12-bis-phenylurethane)".
(8) Z. Iqbal, R. R. Chance, and R. H. Baughman, *J. Chem. Phys.*, **66**, 5520 (1977).
(9) A. J. Melveger and R. H. Baughman, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 603 (1973).
(10) B. Reimer, H. Bässler, J. Hesse, and G. Weiser, *Phys. Status Solidi B*, **73**, 709 (1976); B. Reimer, H. Bässler, and T. Debaerdemaeker, *Chem. Phys. Lett.*, **43**, 85 (1976).
(11) D. Bloor, F. H. Preston, D. J. Ando, and G. C. Stevens, *Chem. Phys. Lett.*, **24**, 407 (1974); D. Bloor, F. H. Preston, and D. J. Ando, *ibid.*, **38**, 33 (1976); D. Bloor and F. H. Preston, *Phys. Status Solidi A*, **37**, 427 (1976).
(12) C. J. Eckhardt, H. Müller, J. Tylicki, and R. R. Chance, *J. Chem. Phys.*, **65**, 4311 (1976).
(13) C. Sauteret, J. Hermann, R. Frey, F. Pradère, J. Ducuing, R. H. Baughman, and R. R. Chance, *Phys. Rev. Lett.*, **36**, 956 (1976).
(14) W. Schermann and G. Wegner, *Makromol. Chem.*, **175**, 667 (1974).
(15) R. R. Chance and R. H. Baughman, *J. Chem. Phys.*, **64**, 3889 (1976); R. R. Chance, R. H. Baughman, P. J. Reucroft, and K. Takahashi, *Chem. Phys.*, **13**, 181 (1976).
(16) B. Reimer and H. Bässler, *Phys. Status Solidi A*, **32**, 435 (1975); K. Lochner, B. Reimer, and H. Bässler, *Chem. Phys. Lett.*, **41**, 388 (1976); B. Reimer and H. Bässler, *ibid.*, **43**, 81 (1976).
(17) D. Bloor, L. Koski, G. C. Stevens, F. H. Preston, and D. J. Ando, *J. Mater. Sci.*, **10**, 1678 (1975).
(18) G. C. Stevens and D. Bloor, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 2411 (1975).
(19) See, for example, G. Kortüm, "Reflectance Spectroscopy", Springer-Verlag New York, New York, N.Y., 1969.
(20) See, for example, R. J. H. Clark, *J. Chem. Educ.*, **41**, 489 (1964).
(21) G. Kortüm, *Trans. Faraday Soc.*, **58**, 1624 (1962); *Angew. Chem., Int. Ed. Engl.*, **2**, 333 (1963), and references cited therein.
(22) K. Yamaoka, Y. Matsuoka, and M. Miura, *J. Phys. Chem.*, **78**, 1040 (1974).
(23) G. Kortüm, M. Kortüm-Seiler, and S. D. Barley, *J. Phys. Chem.*, **66**, 2439 (1962).
(24) N. Takezawa and H. Kobayashi, *Bull. Chem. Soc. Jpn.*, **48**, 2250 (1975).
(25) P. Kubelka and F. Munk, *Z. Tech. Phys.*, **12**, 513 (1931); P. Kubelka, *J. Opt. Soc. Am.*, **38**, 448 (1948).
(26) For a review, see, W. W. Wendlandt, Ed., "Modern Aspects of Reflectance Spectroscopy", Plenum Press, New York, N.Y., 1968; H. G. Hecht, *J. Res. Natl. Bur. Stand., Sect. A*, **80**, 567 (1976).
(27) H. G. Hecht, *Anal. Chem.*, **48**, 1775 (1976).
(28) See, for example, H. Zeitlin and A. Nimoto, *Nature (London)*, **181**, 1616 (1958).
(29) A. S. Makas, *J. Opt. Soc. Am.*, **52**, 43 (1962); W. E. Rense, *ibid.*, **40**, 55 (1950).
(30) See for example, I. A. Drabkin, V. I. Tsaryuk, M. I. Cherkasbln, P. P. Kisilitsa, M. G. Chauser, A. N. Chigir, and A. A. Berlin, *Vysokomol. Soedin., Ser. A*, **10**, 1727 (1968).
(31) H. Kuhn, *Fortschr. Chem. Org. Naturst.*, **16**, 169 (1958); **17**, 404 (1959).
(32) R. H. Baughman and R. R. Chance, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 2037 (1976).
(33) F. Feictmayer, E. Heilbronner, A. Nürrenbach, H. Pommer, and J. Schlag, *Tetrahedron*, **25**, 5383 (1969).
(34) A. F. Preziosi, unpublished results.
(35) G. N. Patel, unpublished results.
(36) V. K. Mitra, W. M. Risen and R. H. Baughman, *J. Chem. Phys.*, **66**, 2731 (1977).
(37) R. R. Chance, R. H. Baughman, A. F. Preziosi, and E. A. Turi, *Bull. Am. Phys. Soc.*, **22**, 408 (1977).
(38) R. R. Chance, A. Prock, and R. Silbey, *J. Chem. Phys.*, **65**, 2527 (1976); 66, 1765 (1977); *Adv. Chem. Phys.*, to be published.
(39) M. Born and E. Wolf, "Principles of Optics", Pergamon Press, Elmsford, N.Y., 1970.

Structure of Imerubrine, a Novel Condensed Tropolone–Isoquinoline Alkaloid

J. V. Silverton,*[1a] C. Kabuto,[1a] Keith T. Buck,[1b] and Michael P. Cava[1b]

Contribution from the Laboratory of Chemistry, NHLBI,
National Institutes of Health, Bethesda, Maryland 20014, and
the Department of Chemistry, University of Pennsylvania,
Philadelphia, Pennsylvania 19104.

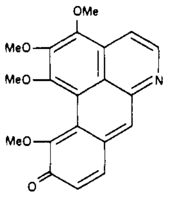
Received May 26, 1977

Abstract: Imerubrine, $C_{20}H_{17}NO_5$, is an orange-red base obtained from *Abuta imene* and *Abuta refescens*. It crystallizes in space group $P\bar{1}$; cell dimensions $a = 11.368$ (1) A°, $b = 11.871$ (1) A°, $c = 13.058$ (1) A°, $\alpha = 94.23$ (1) °, $\beta = 100.87$ (1) °, $\gamma = 75.18$ (1) °. There are four molecules in the unit cell. The structure, solved by a novel direct methods approach, proves to be a new tropolone ether for which the general term "tropoloisoquinoline" is proposed. The possible biosynthesis is discussed.

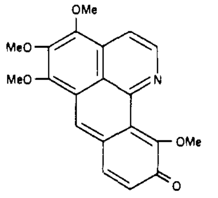
Imerubrine, $C_{20}H_{17}NO_5$, is an orange-red base which has been isolated from the tropical American vines *Abuta imene* and *Abuta refescens*. On the basis of its spectroscopic properties, the tentative structures **1** or **2** were suggested for imerubrine.[2] We now report the results of a complete x-ray crystallographic analysis which shows that imerubrine has neither of these structures, but has instead the remarkable tropolone ether structure **3**. Imerubrine is thus the first example of a new isoquinoline alkaloid type, for which the general term "tropoloisoquinoline" is proposed.[3]

Table I. Crystal and Experimental Data for Imerubrine

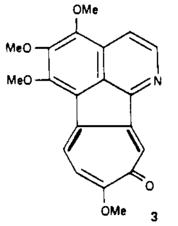
Molecular formula: $C_{20}H_{17}NO_5$	$Z = 4$
Molecular weight: 351.4	$D_m = 1.38$ g cm^{-1}
Habit: prismatic	$D_x = 1.395$ g cm^{-1}
Radiation: Cu Kα (graphite monochromator)	Crystal size: 0.44 × 0.25 × 0.10 mm^3
Wavelength: 1.5418 Å	Reflections: 5678 (1256 unobsd, 1 σ).
Space group: $P\bar{1}$	Maximum sin θ/λ: 0.587 Å^{-1}
Cell dimensions, from LS refinement of $\pm\theta$ data	Diffractometer: Nonius CAD-4 Function minimized: $\Sigma w\Delta^2$
$a = 11.368$ (1) Å	LS weighting: after Peterson and Levy[5]
$b = 11.871$ (1) Å	R (obsd only): 0.040
$c = 13.058$ (1) Å	Anisotropic temperature factor: $\exp[-2\pi^2(\Sigma_i\Sigma_j U_{ij}a^*_i a^*_j h_i h_j)]$
$\alpha = 94.23$ (1) °	
$\beta = 100.87$ (1) °	
$\gamma = 75.18$ (1) °	
$V = 1672.38$ Å^3	



1



2



3

Experimental Section

The crystal system was determined as triclinic. In general all experimental techniques were standard for this laboratory and have been described previously.[4] Further details are given in Table I. Unless otherwise stated, programs used were from the XRAY72[6] system and scattering factors used were those provided.

There was, of course, some doubt about the space group but $P\bar{1}$ was assumed and appears confirmed by the successful refinement. Data collection was routine although there appeared to be some radiation damage. The falloff of intensity standards was 9% from the beginning to the end of the data collection. Lorentz and polarization corrections were applied but not absorption corrections. The distribution of E values appeared hypercentric (instead of the 0.27%, expected for a centrosymmetric structure, 1% of the E values exceed 3.0 and the largest, $E(3,\bar{5},0)$, was 7.3 which may be compared with $E(0,0,0)$:11.0). A Patterson synthesis was compatible with aromatic molecules lying approximately parallel to $(3,\bar{5},0)$ but was not immediately interpretable.

Symbolic addition by means of local semiautomatic programs[7] did not produce a recognizable solution. Many trials were also made with the use of NQEST[8] as a guide in symbolic addition but without useful result. Several attempts were also made to solve the structure using MULTAN[9] with both automatic starts and controlled sets of starting phases but results were similar to those obtained by symbolic addition. The ORTRAN[10] program of Thiessen and Busing was then applied with a view to eliminating unreliable triplets but again unsuccessfully. However, the results of ORTRAN suggested that there were two positions, differing by a rotation of a little less than 30° where the best fit of a benzene ring transform might occur. The information was used to apply Laing's[11] technique, but neither of the two orientations from ORTRAN gave a useful starting set, mainly because there were no strongly interacting planes corresponding to intermolecular vectors.

At this point, we came to the conclusion that our previous starting sets of symbols might be divisible into two weakly or inconsistently interacting subsets corresponding to the two independent molecules. If the angle between the molecules was about 30°, the points where a fitted benzene transform was negative would correspond not only to negative values for one molecule but also to points where the transform of the benzene rings of the second molecule was positive. Any triplets of planes with one or all transform values negative would, following Thiessen and Busing,[10] be unreliable, and it seemed possible that many triplets with large A values which connected the sets might well be unreliable. All planes with E values >2.3 which had negative transform values were then removed and the multisolution approach, using MULTAN, was then applied to the remaining planes. All Σ_1 indications were ignored and, while "MULTAN had trouble defining the

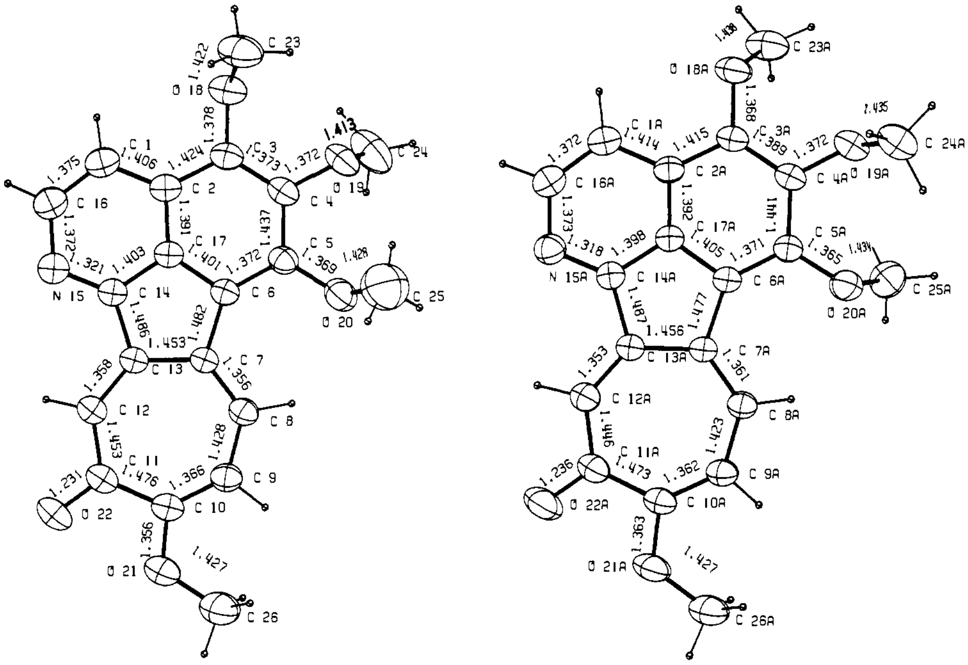


Figure 1. The two independent molecules in their crystal conformations. The two molecules are drawn with 40% probability ellipsoids for the heavier atoms and arbitrary spheres for hydrogen. The molecules are drawn with the coordinates of Table II but, of course, given the center of symmetry, the orientation of the methoxyl groups is actually very similar but not identical (the differences are significant). Estimated standard deviations lie between 0.002 and 0.003 Å for atoms in the nuclei and are <0.004 Å for O-C (methyl) bonds.

Table II. Parameters for the Heavier Atoms (× 10^4)

Atom	*x/a*	*y/b*	*z/c*	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
C(1)	3554 (2)	7070 (2)	8347 (2)	501 (10)	436 (9)	658 (11)	−195 (9)	92 (9)	−60 (8)
C(2)	4359 (2)	7555 (1)	7926 (1)	420 (9)	344 (9)	507 (10)	−69 (8)	74 (8)	−60 (7)
C(3)	4465 (2)	7650 (1)	6868 (1)	441 (9)	455 (9)	469 (10)	−84 (8)	22 (8)	−107 (7)
C(4)	5294 (2)	8210 (2)	6633 (1)	473 (9)	533 (10)	378 (9)	−59 (8)	58 (8)	−30 (7)
C(5)	6095 (2)	8701 (1)	7424 (1)	409 (9)	523 (10)	427 (9)	−126 (8)	84 (8)	10 (7)
C(6)	6038 (1)	8594 (1)	8452 (1)	358 (8)	384 (9)	399 (8)	−63 (7)	74 (7)	−15 (7)
C(7)	6652 (1)	8992 (1)	9468 (1)	368 (8)	335 (8)	382 (8)	−51 (7)	67 (6)	1 (6)
C(8)	7589 (2)	9533 (1)	9623 (1)	449 (9)	484 (9)	423 (9)	−155 (8)	78 (7)	4 (7)
C(9)	8199 (2)	9949 (2)	10578 (1)	451 (9)	510 (10)	495 (10)	−186 (8)	35 (8)	−2 (7)
C(10)	8021 (2)	9932 (1)	11582 (1)	467 (9)	401 (9)	455 (9)	−84 (8)	3 (8)	−28 (7)
C(11)	7129 (2)	9454 (1)	11990 (1)	553 (10)	389 (9)	406 (9)	−35 (8)	57 (8)	3 (7)
C(12)	6263 (2)	8893 (1)	11313 (1)	494 (10)	383 (9)	412 (9)	−91 (8)	113 (8)	12 (7)
C(13)	6063 (1)	8685 (1)	10266 (1)	374 (8)	310 (8)	406 (8)	−35 (7)	65 (7)	23 (6)
C(14)	5120 (1)	8073 (1)	9728 (1)	411 (8)	326 (8)	445 (8)	−69 (7)	92 (7)	6 (7)
N(15)	4355 (1)	7635 (1)	10128 (1)	517 (8)	471 (8)	549 (8)	−170 (7)	155 (7)	29 (7)
C(16)	3588 (2)	7130 (1)	9408 (2)	580 (11)	516 (11)	681 (12)	−258 (9)	174 (10)	9 (9)
C(17)	5161 (1)	8040 (1)	8659 (1)	384 (8)	331 (8)	436 (8)	−70 (7)	82 (7)	−19 (7)
O(18)	3730 (1)	7154 (1)	6099 (1)	576 (7)	667 (8)	577 (7)	−194 (7)	−45 (6)	−171 (6)
O(19)	5309 (1)	8378 (1)	5607 (1)	623 (8)	815 (9)	361 (7)	−84 (7)	81 (6)	−26 (6)
O(20)	6927 (1)	9236 (1)	7163 (1)	602 (7)	894 (9)	480 (7)	−347 (7)	105 (6)	97 (7)
O(21)	8705 (1)	10402 (1)	12382 (1)	642 (8)	700 (8)	479 (7)	−262 (7)	−8 (6)	−91 (6)
O(22)	7104 (1)	9532 (1)	12930 (1)	809 (10)	780 (9)	369 (7)	−242 (8)	71 (6)	−19 (6)
C(23)	2686 (2)	7963 (2)	5565 (2)	589 (15)	984 (19)	714 (17)	−126 (14)	−162 (13)	−159 (15)
C(24)	6178 (3)	7540 (3)	5127 (2)	956 (22)	1362 (29)	571 (15)	192 (20)	362 (15)	40 (16)
C(25)	6404 (4)	10280 (3)	6592 (3)	1351 (31)	1133 (25)	1137 (27)	−698 (24)	−69 (25)	492 (23)
C(26)	9593 (2)	10970 (2)	12166 (2)	765 (16)	935 (18)	696 (16)	−473 (16)	5 (13)	−142 (14)
C(1A)	8976 (2)	2259 (1)	7709 (1)	499 (10)	506 (10)	493 (8)	−227 (8)	27 (8)	−33 (9)
C(2A)	9933 (1)	2811 (1)	7679 (1)	400 (9)	388 (8)	404 (8)	−94 (7)	40 (7)	6 (6)
C(3A)	10430 (2)	3025 (1)	6818 (1)	448 (9)	475 (9)	344 (8)	−111 (8)	32 (7)	−17 (7)
C(4A)	11352 (1)	3626 (1)	6974 (1)	481 (9)	470 (9)	342 (8)	−129 (8)	128 (7)	2 (7)
C(5A)	11880 (1)	3980 (1)	8000 (1)	419 (9)	410 (8)	397 (8)	−159 (7)	115 (7)	−3 (6)
C(6A)	11417 (1)	3771 (1)	8844 (1)	378 (8)	325 (8)	348 (8)	−84 (7)	77 (6)	0 (6)
C(7A)	11680 (1)	3991 (1)	9982 (1)	362 (8)	314 (7)	350 (8)	−68 (7)	78 (6)	2 (6)
C(8A)	12565 (1)	4505 (1)	10511 (1)	422 (9)	423 (9)	396 (8)	−141 (7)	97 (7)	5 (7)
C(9A)	12839 (2)	4758 (1)	11599 (1)	424 (9)	500 (10)	400 (9)	−152 (8)	53 (7)	−46 (7)
C(10A)	12329 (2)	4551 (1)	12408 (1)	431 (9)	511 (9)	349 (8)	−53 (8)	53 (7)	−46 (7)
C(11A)	11346 (2)	3945 (1)	12401 (1)	463 (10)	602 (10)	370 (9)	−81 (8)	135 (7)	23 (7)
C(12A)	10680 (2)	3545 (1)	11447 (1)	445 (9)	488 (9)	417 (9)	−154 (8)	148 (7)	10 (7)
C(13A)	10821 (1)	3548 (1)	10441 (1)	360 (8)	340 (8)	377 (8)	−65 (7)	95 (6)	15 (6)
C(14A)	10050 (1)	3050 (1)	9566 (1)	376 (8)	371 (8)	418 (8)	−104 (7)	110 (7)	25 (6)
N(15A)	9161 (1)	2534 (1)	9601 (1)	492 (8)	545 (8)	509 (8)	−232 (7)	127 (7)	14 (6)
C(16A)	8636 (2)	2158 (2)	8646 (1)	506 (10)	587 (11)	589 (11)	−304 (9)	82 (9)	7 (8)
C(17A)	10445 (1)	3210 (1)	8648 (1)	360 (8)	343 (8)	382 (8)	−80 (7)	78 (6)	14 (6)
O(18A)	9902 (1)	2696 (1)	5850 (1)	560 (7)	795 (8)	364 (6)	−218 (7)	8 (5)	−91 (6)
O(19A)	11804 (1)	3841 (1)	6125 (1)	676 (8)	631 (8)	383 (6)	−210 (6)	208 (6)	17 (5)
O(20A)	12776 (1)	4582 (1)	8129 (1)	571 (7)	661 (7)	481 (7)	−347 (6)	201 (6)	−80 (5)
O(21A)	12707 (1)	4901 (1)	13406 (1)	596 (8)	890 (9)	354 (6)	−227 (7)	65 (6)	−121 (6)
O(22A)	11073 (1)	3778 (1)	13240 (1)	764 (10)	1209 (12)	382 (7)	−398 (9)	187 (6)	18 (7)
C(23A)	10707 (2)	1953 (2)	5215 (2)	749 (15)	889 (17)	513 (13)	−153 (14)	47 (11)	−250 (12)
C(24A)	11505 (2)	5034 (2)	5823 (2)	811 (16)	694 (14)	503 (12)	−150 (12)	177 (11)	197 (10)
C(25A)	13912 (2)	4018 (2)	7781 (2)	469 (12)	797 (16)	778 (15)	−200 (11)	143 (11)	105 (12)
C(26A)	13710 (2)	5449 (2)	13636 (2)	653 (14)	846 (16)	483 (12)	−262 (13)	21 (10)	−138 (11)

origin", with six variable phases, the set of phases expanded readily.

Of the 64 solutions, the one with the highest combined figure of merit proved correct and all but four atoms of the two molecules were visible in the *E* map. For the record, the other figures of merit were ABSFOM, 1.0575 (13th highest); PSIZERO, 0.2967 × 10^3 (2nd lowest); and R_k, 26.83% (2nd lowest, the lowest, of course, being the solution with all signs +).

Standard refinement techniques finally resulted in an *R* factor of 0.040 (observed reflexions only) using anisotropic thermal parameters for the heavier atoms and isotropic thermal parameters for hydrogen atoms (considerable partitioning of the least-squares matrix was necessary given the size of the problem but the process converged satisfactorily). Atomic parameters are given in Tables II and III. A table of structure factors is available as supplemental material (see paragraph at end of paper for details).

Discussion

Molecular Structure. The bond lengths for the two molecules are given in Figure 1 (an ORTEP[12] diagram), bond angles in Table IV, and a packing diagram as Figure 2. It will be noted that the agreement in the bond lengths of the two independent molecules is very satisfactory. Standard deviations of bond lengths, from the least-squares calculation, range from 0.002 to 0.004 Å with an average of 0.0035 Å and the actual average standard deviation, assuming the molecules are truly identical, is 0.005 Å.

The two molecular nuclei are coplanar to within about 2° but are twisted by ~21° around their plane normals. Neither 17-atom nucleus is planar on the χ^2 test, although individual rings are essentially planar and overall deviations are small. The slightly different conformations of the two independent nuclei are probably a consequence of packing forces. The two tropolone rings are essentially planar, although some deviations, particularly that of C(11A), 0.03 Å, are statistically significant.

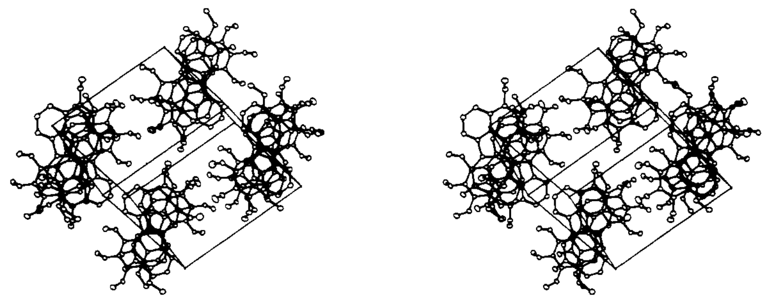


Figure 2. Packing diagram, the direction of projection is onto the plane of the molecule containing C(1).

Table III. Parameters for the Hydrogen Atoms (× 10^3). Designations Indicate Attachments

Atom	x/a	y/b	z/c	U	Atom	x/a	y/b	z/c	U
1	298 (1)	672 (1)	789 (1)	69	1A	854 (1)	194 (1)	705 (1)	59
8	790 (1)	967 (1)	897 (1)	50	8A	1306 (1)	478 (1)	1010 (1)	42
9	884 (1)	1035 (1)	1047 (1)	51	9A	1350 (1)	514 (1)	1180 (1)	47
12	576 (1)	860 (1)	1171 (1)	39	12A	1003 (1)	320 (1)	1159 (1)	45
16	301 (1)	678 (1)	967 (1)	68	16A	795 (1)	180 (1)	870 (1)	50
231	222 (2)	755 (2)	515 (2)	110	231A	1024 (2)	134 (2)	487 (1)	117
232	220 (3)	848 (2)	604 (2)	152	232A	1148 (2)	151 (2)	563 (2)	112
233	295 (3)	837 (3)	505 (3)	208	233A	1086 (2)	240 (2)	466 (2)	153
241	698 (3)	736 (2)	564 (2)	176	241A	1207 (2)	550 (2)	631 (2)	155
242	628 (3)	784 (2)	457 (2)	133	242A	1161 (2)	506 (1)	511 (1)	101
243	568 (4)	675 (4)	498 (3)	264	243A	1063 (2)	543 (2)	592 (1)	125
251	576 (3)	1029 (3)	606 (3)	165	251A	1379 (2)	329 (2)	736 (2)	146
252	624 (4)	1090 (3)	715 (3)	230	252A	1453 (3)	386 (2)	839 (2)	185
253	705 (4)	1042 (3)	643 (3)	189	253A	1418 (2)	455 (2)	740 (2)	144
261	996 (2)	1127 (2)	1287 (2)	120	261A	1446 (2)	490 (1)	1348 (1)	82
262	1027 (2)	1040 (2)	1188 (2)	123	262A	1354 (1)	618 (1)	1323 (1)	78
263	916 (2)	1166 (2)	1166 (2)	112	263A	1379 (1)	562 (1)	1440 (1)	77

Table IV. Bond Angles. Estimated Standard Deviations Range from 0.10 to 0.18°. The Second Set of Angles Refers to the Atoms with the Suffix A

2	1	16	119.6	119.6	9	10	O21	121.3	122.1
1	2	3	130.2	129.8	11	10	O21	109.4	108.7
1	2	17	114.8	114.2	10	11	12	122.1	122.5
3	2	17	115.0	116.0	10	11	O22	119.5	118.9
2	3	4	120.2	119.6	12	11	O22	118.4	118.7
2	3	O18	118.4	117.3	11	12	13	132.1	131.5
4	3	O18	121.4	122.9	7	13	12	129.9	130.5
3	4	5	122.3	122.0	7	13	14	107.0	106.6
3	4	O19	119.3	118.6	12	13	14	123.1	122.9
5	4	O19	118.2	119.4	13	14	N15	129.1	128.7
4	5	6	118.7	119.0	13	14	17	107.0	107.3
4	5	O20	120.9	120.7	N15	14	17	123.9	124.0
6	5	O20	120.4	120.1	14	N15	16	114.3	114.2
5	6	7	135.5	135.8	1	16	N15	125.7	125.8
5	6	17	117.1	117.2	2	17	6	126.6	126.1
7	6	17	107.3	107.0	2	17	14	121.7	122.1
6	7	8	126.5	126.6	6	17	14	111.7	111.8
6	7	13	106.9	107.4	3	O18	23	114.3	117.4
8	7	13	126.6	126.0	4	O19	24	116.6	116.5
7	8	9	128.8	128.8	5	O20	25	115.6	117.4
8	9	10	131.2	131.2	10	O21	26	119.3	119.8
9	10	11	129.3	129.3					

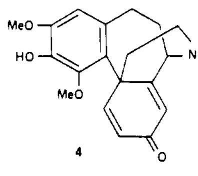
Table V. Comparison of Average Values (Ångstroms) for Tropolone Bond Lengths (Calculated from the References Given by Karlsson, Pilotti, and Wiehager[13]) with the Averaged Values for the Present Structure. The Numbering Corresponds to that of Tropolone Itself, C(1) Being the Atom Attached to the Carbonyl Oxygen Atom and Proceeding through the Carbon Atom Attached to the Second Oxygen Atom

	C(1)-O(1)	C(2)-O(2)	C(1)-C(2)	C(2)-C(3)	C(3)-C(4)	C(4)-C(5)	C(5)-C(6)	C(6)-C(7)	C(7)-C(1)
Average from literature	1.252	1.342	1.464	1.368	1.409	1.367	1.415	1.365	1.426
Average from present structure	1.233	1.359	1.475	1.364	1.425	1.358	1.454	1.355	1.449

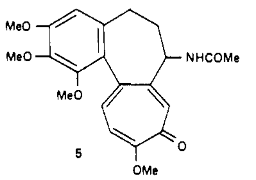
The alternation of ring bond lengths, previously noted in tropolones, is again apparent. A set of average values calculated from ref 13 is compared in Table V with the average values in imerubrine and it will be seen that values are very similar except perhaps for C(1)-O(1) which is definitely shorter in imerubrine and C(5)-C(6) which, in imerubrine, is fused to the five-membered ring and is definitely longer than the average values. It would seem that the enhanced possibilities of conjugation in imerubrine and the larger delocalized system, also betokened by the red color, have not greatly affected the resonance forms of unsubstituted tropolone.

The molecular packing is shown in Figure 2. Intermolecular distances, in general, correspond to van der Waals interactions and only two distances are worthy of note: the methyl carbon atom, C(24A), is 3.23 Å from the carbonyl oxygen atom, O(22A), in a molecule related by a center of symmetry and O(19A) is 3.12 Å from the methoxyl carbon atom, C(24).

Stacks of approximately parallel molecules, arranged directly above each other, extend through the crystal. The mean planes of the 17 nuclear atoms of the two molecules have equations, in crystal coordinates, $-5.329x + 8.670y - 0.196z = 4.096$ and $-5.062x + 8.450y - 0.625z = 2.058$ ("A" molecule). The dihedral angle between the planes is 2.18°. Plane (3,$\bar{5}$,0), which has the equation $-5.250x + 8.750y + 0.000z = -1.750$, makes dihedral angles of 1.09 and 2.75°, respectively, with the two nuclear planes.

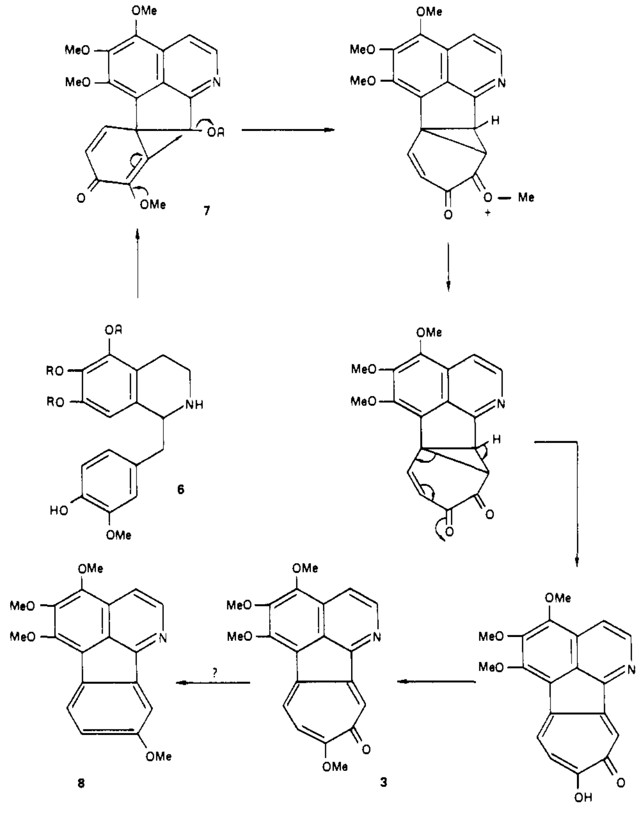


4



5

Scheme I



The distances of the molecules in the stacks, denoting the first molecule by O, the second by A, and the operation of the center of symmetry by a prime, are O-O′, 3.43 Å; O′-A, 3.53 Å; and A-A′, 3.48 Å. The molecular packing is somewhat unusual for aromatic molecules and might almost suggest a charge-transfer complex, but the intermolecular distances are not particularly short.

Biogenetic Considerations. Colchicine (**5**) and its congeners represent the only previously known group of alkaloids containing a tropolone system.[14] Biosynthetic studies have shown that the tropolone ring of colchicine arises from the dienone system of androcymbine (**4**) by way of a fused cyclopropane intermediate.[15]

We propose that imerubrine probably originates by a related pathway, as outlined in Scheme I. The intermediate dienone (**7**) is simply a highly oxidized proaporphine, and, since proaporphines are intramolecular oxidative coupling products of benzyltetrahydroisoquinolines (i.e., **6**),[16] imerubrine can be rationalized as a new type of oxidative transformation product of a benzyltetrahydroisoquinoline. Knowledge of the structure of imerubrine also suggests that the azafluoranthenes which accompany imerubrine in the same plants may be in fact derived from tropoloisoquinoline precursors, rather than from phenylisoquinolines as proposed earlier. Thus, conversion of imerubrine (**3**) to the azafluoranthene rufescine (**8**)[2,17] involves only a formal decarbonylation of the tropolone ring of **3**.

Supplemental Material Available: Structure factor table (33 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Laboratory of Chemistry, NHLBI, NIH, Bethesda, Md. (b) Department of Chemistry, University of Pennsylvania, Philadelphia, Pa.
(2) M. P. Cava, K. T. Buck, I. Noguchi, M. Srinivasan, and A. I. DaRocha, *Tetrahedron*, **31**, 1667 (1975).
(3) The systematic name for the ring system found in this alkaloid is azuleno[1,2,3-*i,j*]isoquinoline.
(4) J. V. Silverton and H. A. Lloyd, *Acta Crystallogr., Sect. B*, **31**, 1576 (1975).
(5) S. W. Peterson and H. A. Levy, *Acta Crystallogr.*, **10**, 70 (1957).
(6) J. M. Stewart, G. J. Kruger, H. L. Ammon, C. Dickinson, and S. R. Hall, "The X-ray system", Technical Report TR-102, Computer Center, University of Maryland, 1972.
(7) J. V. Silverton, *Acta Crystallogr., Sect. B*, **29**, 293 (1973).
(8) G. T. De Titta, J. E. Edmonds, D. A. Langs, and H. Hauptman, *Acta Crystallogr., Sect. A*, **31**, 472 (1975).
(9) MULTAN, a computer program for the automatic solution of crystal structures: P. Main, M. M. Woolfson, and G. Germain, Universities of York and Louvain, 1971.
(10) W. E. Thiessen and W. R. Busing, *Acta Crystallogr., Sect. A*, **30**, 814 (1973).
(11) M. Laing, *Acta Crystallogr., Sect. A*, **32**, 673 (1976).
(12) ORTEP: C. K. Johnson, Oak Ridge National Laboratory Report ORNL-3794, 1965.
(13) B. Karlsson, A. M. Polotti, and A. C. Wiehager, *Acta Crystallogr., Sect. B*, **32**, 3118 (1976), and references cited there.
(14) T. Kametani, Ed., "The Chemistry of Isoquinoline Alkaloids", Elsevier Publishing Co., New York, N.Y., 1969, pp 222-226.
(15) A. R. Battersby, *Pure Appl. Chem.*, **14**, 117 (1967).
(16) M. Shamma, "The Isoquinoline Alkaloids, Chemistry and Pharmacology", Academic Press, New York, N.Y., 1972, 185.
(17) M. P. Cava, K. T. Buck, and A. I. DaRocha, *J. Am. Chem. Soc.*, **94**, 5931 (1972).