

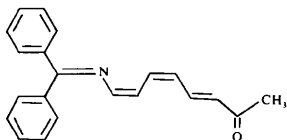
(3*E*,5*Z*,7*Z*)-8-(Diphenylmethylene)amino-3,5,7-octatrien-2-one*

BY ROSALIND Y. WONG

Western Regional Research Laboratory, Science and Education Administration, US Department of Agriculture, Berkeley, California 94710, USA

(Received 16 February 1978; accepted 6 June 1978)

Abstract. $C_{21}H_{19}NO$, orthorhombic, *Pbca*, $a = 14.547(5)$, $b = 9.439(4)$, $c = 25.922(6)$ Å, $Z = 8$, $D_c = 1.124$ g cm⁻³, Cu $K\alpha$ radiation, $\lambda = 1.5418$ Å, $\mu = 5.39$ cm⁻¹. The structure was solved by direct methods. Least-squares refinement gave $R_1 = 0.0503$ for 911 independent observed reflections [$I \geq \sigma(I)$]. The structural formula of the molecule is:



Introduction. The title compound, an enamine Schiff base, was synthesized from diphenyldichloromethane, pyridine, acetone and base as a model intermediate in the preparation of complex polyenes such as insect pheromones. The present X-ray results confirm the structure derived from chemical analysis (Molyneux & Wong, 1977).

Orange prismatic crystals of the title compound were grown from a mixture of methanol and water. Weissenberg and precession photographs show systematic absences $0kl$ with $k = 2n + 1$, $h0l$ with $l = 2n + 1$, and $hk0$ with $h = 2n + 1$ which indicate the space group *Pbca*. Lattice parameters were obtained by averaging the results obtained from high-angle θ - 2θ scans. A prismatic crystal $0.15 \times 0.38 \times 0.10$ mm was used to collect intensities with an IBM-1800 controlled automatic GE† diffractometer at room temperature with Ni-filtered Cu radiation. Because the data were poor owing to radiation damage, they were only recorded up to $2\theta = 80^\circ$, using the θ - 2θ scan technique with a scan rate of 1° min⁻¹. Additional details about the method of data collection and reduction have been described previously (Wong, Palmer & Manners, 1976). 2091 reflections were measured of which 1072 were unique; of these, 34 reflections were measured as zero and 127 others had $I \leq \sigma(I)$. These 161 reflections were

excluded from the least-squares refinements. The intensities of two standard reflections, measured at regular intervals, showed no significant changes during the course of the experiment. Intensity data were corrected for Lorentz-polarization but not for absorption; $\mu = 5.39$ cm⁻¹ for Cu $K\alpha$. A correction for secondary extinction was applied during the final stages of refinement as discussed below.

The crystal structure was solved by direct methods using the *MULTAN* program (Germain, Main & Woolfson, 1971). An *E* Fourier synthesis revealed the parameters of the 23 heavy atoms. The nineteen H atoms were located on a difference Fourier map. The positional and thermal parameters were refined by a full-matrix least-squares program which minimizes the function $\sum w(\Delta F)^2$ where $\Delta F = |F_o| - |F_c|$. The weighting factor w was taken equal to $1/\sigma^2(F)$, where $\sigma(F) = F_o - [F_o^2 - \sigma(F_o^2)]^{1/2}$, when $I \geq \sigma(I)$ and equal to zero otherwise. Refinement with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors, with restriction on the atomic coordinates, for H atoms gave a discrepancy index R_1 , defined as $\sum ||F_o| - |F_c|| / \sum |F_o|$, of 0.0515. A comparison of the observed and calculated structure factors for the most intense reflections indicated that a secondary-extinction correction was necessary (Zachariasen, 1963). An extinction coefficient of 1×10^{-7} was found to minimize the discrepancy between F_o and F_c and led to a small, but significant, improvement in R_1 . The final discrepancy index R_1 is 0.0503 for 911 data and 0.0629 for all 1072 data. $R_2 = (\sum w|\Delta F|^2 / \sum w|F_o|^2)^{1/2} = 0.0553$ and the standard deviation of an observation of unit weight is 1.520. All parameter shifts for non-hydrogen atoms in the final cycle of least-squares refinement were less than 0.5σ . Scattering factors for all atoms except H were taken from Cromer & Waber (1965). The H scattering factors were those of Stewart, Davidson & Simpson (1965). Final positional parameters are given in Table 1.†

* The atomic numbering and conformational notation used in this paper conform to the alternative description of the title compound: (3*Z*,5*Z*,7*E*)-1,1-diphenyl-2-aza-1,3,5,7-decatetraen-9-one.

† Reference to a company and/or product named by the Department is only for purposes of information and does not imply approval or recommendation of the product to the exclusion of others which may also be suitable.

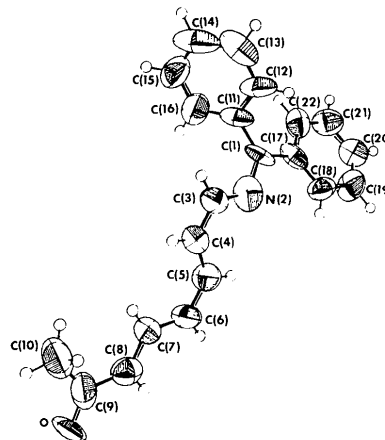
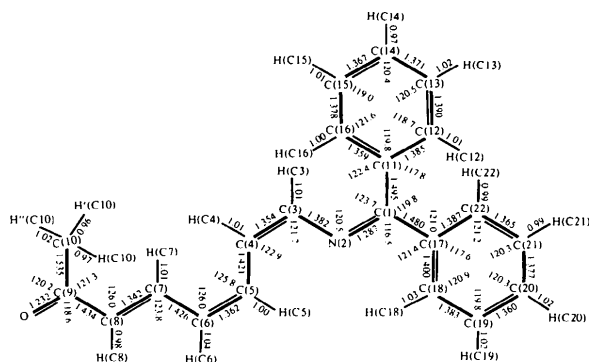
† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33683 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Positional parameters ($\times 10^4$) with their estimated standard deviations in parentheses

The positional parameters of the H atoms were not refined.

	x	y	z
O	5290 (3)	-650 (5)	4010 (2)
N(2)	1643 (3)	2243 (5)	1542 (2)
C(1)	1386 (4)	2757 (7)	1106 (3)
C(3)	2315 (5)	1210 (7)	1564 (3)
C(4)	2731 (3)	856 (5)	2013 (3)
C(5)	2533 (4)	1542 (6)	2489 (3)
C(6)	2986 (5)	1335 (6)	2942 (3)
C(7)	3743 (4)	400 (6)	3022 (3)
C(8)	4175 (5)	246 (6)	3476 (3)
C(9)	4971 (5)	-612 (8)	3570 (3)
C(10)	5429 (6)	-1460 (9)	3134 (3)
C(11)	1863 (5)	2459 (6)	607 (3)
C(12)	1373 (5)	1757 (7)	227 (4)
C(13)	1810 (9)	1443 (9)	-236 (4)
C(14)	2700 (9)	1880 (9)	-324 (3)
C(15)	3172 (6)	2585 (9)	52 (5)
C(16)	2744 (6)	2868 (6)	515 (3)
C(17)	604 (5)	3761 (7)	1118 (3)
C(18)	-12 (6)	3790 (7)	1533 (2)
C(19)	-731 (5)	4747 (9)	1545 (3)
C(20)	-845 (5)	5674 (7)	1148 (4)
C(21)	-239 (7)	5680 (7)	740 (3)
C(22)	473 (5)	4739 (9)	726 (3)
H(C3)	2590	723	1252
H(C4)	3189	57	1984
H(C5)	2045	2283	2534
H(C6)	2732	2004	3225
H(C7)	4014	-218	2744
H(C8)	3867	830	3737
H(C10)	4965	-2190	3129
H'(C10)	5433	-830	2841
H''(C10)	5988	-1994	3270
H(C12)	716	1496	312
H(C13)	1407	902	-489
H(C14)	2985	1673	-653
H(C15)	3828	2860	-20
H(C16)	3133	3383	773
H(C18)	56	3059	1827
H(C19)	-1184	4820	1841
H(C20)	-1373	6390	1148
H(C21)	-339	6368	457
H(C22)	909	4702	433

planes formed by the polyene chain [C(1) to C(10)] and the phenyl rings C(11)–C(16), C(17)–C(22) are 58.1 and 38.1° respectively. The configuration of the conjugated chain is *cis-cis-trans* (3Z,5Z,7E). The average C–C bond lengths and angles of the two aromatic rings are 1.38 \AA and 120° respectively.

Fig. 1. Perspective view of one molecule with 50% probability thermal ellipsoids. An arbitrary temperature factor of 1.0 \AA^2 was assigned to the H atoms.Fig. 2. Bond angles ($^\circ$) and bond lengths (\AA) for the title compound. E.s.d.'s are 0.8° and 0.008 \AA , respectively, for angles and distances between heavy atoms. E.s.d.'s are 0.09 \AA for the distances involving H atoms.

Discussion. The molecular structure of the title compound is shown in Fig. 1 (Johnson, 1965). The atom-numbering system, and intramolecular bond lengths and angles (involving non-hydrogen atoms only) are presented in Fig. 2. The molecule contains three planar segments: the two phenyl rings and the conjugated chain from C(1) to C(10). The near planarity of the side chain is illustrated by the torsion angles between the bond segments listed in Table 2. All atoms in both benzene rings lie within $\pm 0.01 \text{ \AA}$ of their best least-squares plane. The dihedral angle between the two phenyl rings is 78.1° . The observed conformation of the two phenyl rings reduces the steric interaction between H(C12)–H(C22) and H(C3)–H(C16) (Fig. 1). The dihedral angles between the best least-squares

Table 2. Torsion angles ($^\circ$)

Single bonds		Double bonds	
1–2–3–4	13.6	11–1–2–3	9.0
3–4–5–6	6.8	2–3–4–5	2.1
5–6–7–8	0.8	4–5–6–7	0.3
7–6–9–0	0.2	6–7–8–9	3.9
7–8–9–10	0.8		
12–11–1–17	66.6		
16–11–1–2	63.8		
18–17–1–2	20.9		
22–17–1–11	19.4		

The appreciable degree of conjugation between the alternating single and double bonds throughout the polyene chain is apparent with the single bonds (mean = 1.451 Å) slightly shorter and the double bonds (mean = 1.353 Å) slightly longer than for a non-resonating single-bond-double-bond system. This result is in good agreement with other conjugated-chain structures (Gilardi, Karle & Karle, 1972; Bart & MacGillavry, 1968). C(9)–C(10) does not enter into the resonance system as it has the expected single-bond value of 1.54 Å. The bond distances for C(1)–C(11) and C(1)–C(17) suggest that these bonds have less double-bond character than the other single bonds in the conjugated side chain. This results from the restricted resonance between the phenyl rings and the side chain caused by the non-planarity of the phenyl rings with the plane formed by the side chain. The short bond length of 1.287 Å between C(1) and N(2) is consistent with the unambiguous location of the double bond to the N. The carbonyl bond length, 1.232 Å, agrees with the accepted normal value.

The bond angles along the chain, with the exception of those around C(1), N(2) and C(9), show no significant deviation from the mean value of 124.4°. The decreased bond angles opposite the methyl group at C(9) and around C(1) may be due to the steric crowding which would be eased by the observed slight

distortion in bond angles. There are no intermolecular hydrogen bonds or short contact distances between molecules.

I wish to thank Dr K. J. Palmer for his valuable discussions, Dr A. Zalkin for the use of his computer programs and Dr R. J. Molyneux for suggesting the problem and for providing a sample of crystalline material.

References

- BART, J. C. J. & MACGILLAVRY, C. H. (1968). *Acta Cryst.* **B24**, 1569–1587.
 CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
 GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* **A27**, 368–376.
 GILARDI, R. D., KARLE, I. L. & KARLE, J. (1972). *Acta Cryst.* **B28**, 2605–2612.
 JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
 MOLYNEUX, R. J. & WONG, R. Y. (1977). *Tetrahedron*, **33**, 1931–1934.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 WONG, R. Y., PALMER, K. J. & MANNERS, G. D. (1976). *Acta Cryst.* **B33**, 970–974.
 ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1978). **B34**, 3484–3486

2,3-Diphenyl-5-(α -D-lyxofuranosyl)tetrazolium Bromide

BY K. BÖRJE LINDBERG

University of Stockholm, Arrhenius Laboratory, Structural Chemistry, S-106 91 Stockholm, Sweden

AND MÁTYÁS CZUGLER, VIRÁG ZSOLDOS-MÁDY, ISTVÁN PINTÉR AND ANDRÁS MESSMER

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525-Budapest, POB 17, Hungary

(Received 5 July 1977; accepted 25 July 1978)

Abstract. C₁₈H₁₉BrN₄O₄, $M_r = 435.27$, tetragonal, $P4_32_12$, $a = b = 8.4723$ (3), $c = 52.303$ (3) Å, $Z = 8$, $D_x = 1.54$ g cm⁻³. The X-ray analysis corroborates chemical and spectroscopic evidence about the molecular configuration.

Introduction. Pale-yellow crystals of the title compound were obtained by slow evaporation of its water solution under a thin benzene surface. Cell dimensions were obtained from a powder photograph at 20°C taken in a Guinier–Hägg focusing camera with highly monochromatized Cu $K\alpha_1$ radiation ($\lambda = 1.54051$ Å) using

KCl as an internal standard [$a = 6.2919$ (4) Å]. Distances on the film were measured with a SAAB film scanner connected to an IBM 1800 computer and were evaluated using the program *PILT* (Malmros & Werner, 1973). A prismatic specimen (0.45 × 0.45 × 0.15 mm) was mounted on a goniometer head approximately along the c axis. Intensities were collected on a Philips PW 1100 four-circle diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The 2090 independent data available within $0 < \theta < 67^\circ$ were collected with θ – 2θ scans of 1° scan width. Lorentz-polarization and absorption corrections were applied. The crystal structure was solved by the heavy-atom