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Neutron Diffraction at 9 K and *ab-initio* Molecular-Orbital Studies of the Molecular Structure of Glyoxime

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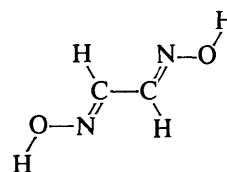
Abstract

The crystal structure of glyoxime, ethanedial dioxime, $C_2H_4N_2O_2$, has been refined using single-crystal neutron diffraction data [$\lambda = 1.0470$ (3) Å] measured at 9 K. The crystal data at 9 K are: $P2_1/c$, $a = 3.745$ (1), $b = 4.398$ (2), $c = 10.852$ (5) Å, $\beta = 92.41$ (3)°, $D_x = 1.638$ Mg m⁻³, $Z = 2$. The final agreement factors for 772 observations were $R(F) = 0.029$, $R(F^2) = 0.027$, $wR(F) = 0.026$, $wR(F^2) = 0.044$, $S = 2.269$. The molecule has crystallographic $\bar{1}$ symmetry and is planar with the exception of the oxime hydrogen atom which is 0.263 (1) Å out of the molecular plane. A rigid-body thermal motion analysis gave a good fit for the non-hydrogen atoms with r.m.s. $\Delta U_{ij} = 0.0004$ Å² and $\sigma(U_{ij}) = 0.0005$ Å². The observed and [corrected] bond lengths (Å) are: C–C 1.4528 (10) [1.455]; C=N 1.2849 (8) [1.288]; N–O 1.3854 (8) [1.388]; C–H 1.0926 (12) [1.107]; O–H 0.9947 (12) [1.010]. *Ab-initio* molecular-orbital calculations were carried out at the Hartree–Fock (HF) STO-3G level on the three most likely minimum-energy conformations of the molecule, two with $\bar{1}$ (C_i) symmetry and one with $2m$ (C_{2v}) symmetry. The conformation observed in the crystal is that of minimum energy calculated for the isolated molecule at rest. The optimized bond lengths, calculated at the HF/3-21G level for the isolated molecule at rest, are: C–C 1.463; C=N 1.258; N–O 1.439; C–H 1.072; O–H 0.967 Å. The larger discrepancies between the

theoretical and experimental values of the bond lengths of -0.030 Å for C=N and $+0.051$ Å for N–O were reduced to -0.012 and $+0.014$ Å when corrections were applied for approximations in the theory, extrapolated from calculations on simple related molecules, and for hydrogen bonding.

Introduction

The crystal structure of glyoxime, $H_2C_2(NO)_2$, was determined by Calleri, Ferraris & Viterbo (1966) by X-rays at room temperature. The molecules have crystallographic $\bar{1}$ symmetry in the *anti-anti-anti* conformation (I). No subsequent experimental or theoretical calculations have been published on this relatively simple molecule. In the present work, a neutron diffraction crystal structure refinement at 9 K is reported. These results are compared with those from *ab-initio* molecular-orbital-geometry optimization for the isolated molecules at rest. This is a continuation of similar comparisons of the experimental and theoretical



(I)

molecular structures of acetamide (Jeffrey, Ruble, McMullan, DeFrees, Binkley & Pople, 1980), monofluoroacetamide (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981a), formamide oxime (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981b), and *N,N'*-diformohydrazide (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1982).

Experimental

The neutron diffraction data collection and structure refinement used the same methods and procedures as described for formamide oxime (Jeffrey, Ruble, McMullan, DeFrees & Pople, 1981b) except for the information provided below.

Crystals of glyoxime were obtained by slow evaporation of an aqueous solution at room temperature. A specimen $2.1 \times 1.6 \times 1.0$ mm cut from a larger plate had faces {100}, {001}, (011) and (0 $\bar{1}$ 1) and weighed 0.00592 g. It was mounted with the *a* axis within 1° of the φ axis of the diffractometer and was cooled at a rate of 1 K min^{-1} to a final temperature of $9.0 \pm 0.5 \text{ K}$, which was maintained during data collection. The lattice parameters, given in Table 1, were determined using 32 reflections with $42 < 2\theta < 55^\circ$. Neutron integrated intensities were measured for *h, k, ±l* using scan widths of $\Delta(2\theta) = 3.6^\circ$ for $\sin \theta/\lambda \leq 0.48 \text{ \AA}^{-1}$, and varied according to the dispersion

formula, $\Delta(2\theta) = 3.630^\circ + 2.247^\circ \tan \theta$ for $0.48 \leq \sin \theta/\lambda < 0.78 \text{ \AA}^{-1}$. Neutron absorption corrections were applied using an analytical procedure (Templeton & Templeton, 1973). The linear absorption coefficient ($\mu = 179.2 \text{ m}^{-1}$) was calculated assuming the mass absorption coefficient for chemically bonded hydrogen to be $2.4835 \text{ m}^2 \text{ kg}^{-1}$ at $\lambda = 1.0470 \text{ \AA}$ (McMullan & Koetzle, 1980). The resulting transmission factors ranged from 0.74 to 0.85. There were nine intensities recorded with negative values; none significantly different from zero.

The initial atomic coordinates for the refinement were from Calleri, Ferraris & Viterbo (1966) with assumed isotropic thermal factors of $U = 0.006 \text{ \AA}^2$ for the non-hydrogen atoms and $U = 0.009 \text{ \AA}^2$ for the hydrogen atoms. The refinement was carried out initially by difference synthesis and then by full-matrix least-squares procedures minimizing the function $\sum w_i |F_o^2 - kF_c^2|^2$, where $w_i = [\sigma_c^2 + (0.01F_o^2)^2]^{-1}$. The scattering lengths used were those given by Koester (1977). After the final cycle of refinement using all 772 recorded observations, there were no changes greater than 0.13σ in any of the parameters. The largest feature in the final difference map was 2.5σ , where σ was estimated from $\sigma(F)$. The final agreement factors were $R(F) = 0.029$, $R(F^2) = 0.027$, $wR(F) = 0.026$, $wR(F^2) = 0.044$, $S = 2.269$. Extinction was severe, with 13% of the reflections significantly attenuated, having $F_o/F_c \leq 0.95$. The greatest extinction was for 006, with $F_o^2/F_c^2 = 0.45$. Anisotropic extinction parameters were included in the refinement assuming a type I crystal with Lorentzian distribution of mosaicity (Becker & Coppens, 1975). The parameters g_{ij} are unusually anisotropic, with $g_{11} = 5.3(2)$ and $g_{33} = 284(27)$. The final atomic parameters are given in Table 2.* The atomic notation and thermal ellipsoids at 75% probability (Johnson, 1976) are shown in Fig. 1.

* Lists of observed and calculated structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36773 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Crystal data for glyoxime, ethanedial dioxime*

	This work (9 K)	Calleri, Ferraris & Viterbo (1966) (293 K)
Formula	$\text{C}_2\text{H}_4\text{N}_2\text{O}_2$; CAS Reg. No. 557-30-2	
Space group	$P2_1/c$; $Z = 2$	
<i>a</i>	3.745 (1) Å	3.868 (11) Å
<i>b</i>	4.398 (2)	4.414 (15)
<i>c</i>	10.852 (5)	10.949 (35)
β	92.41 (3)°	91.17°
D_x	1.638 Mg m ⁻³	1.565 Mg m ⁻³
λ_n	1.0470 (3) Å	

Table 2. *Final atomic parameters for glyoxime at 9 K*

The fractional coordinates are $\times 10^5$ for non-hydrogen atoms, $\times 10^4$ for hydrogen atoms. Anisotropic temperature factors ($\text{\AA}^2 \times 10^4$) are referred to the crystallographic axis and correspond to the temperature-factor expression $T = \exp[-2\pi^2 \sum_i \sum_j h_i h_j a_i^* a_j^* U_{ij}]$. Estimated standard deviations given in parentheses refer to the least significant digit. Anisotropic extinction parameters, *g*, are in $\text{rad}^2 \times 10^8$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C	10240 (13)	13035 (10)	2254 (4)	63 (2)	41 (2)	45 (2)	-3 (1)	3 (1)	-4 (1)
N	6618 (9)	21388 (8)	13478 (3)	67 (1)	46 (1)	46 (1)	-3 (1)	3 (1)	-4 (1)
O	27894 (14)	46164 (13)	16673 (5)	78 (2)	52 (2)	59 (2)	-8 (2)	2 (2)	-12 (2)
H(1)	2800 (3)	2512 (3)	-380 (1)	236 (5)	196 (5)	168 (4)	-67 (4)	65 (4)	4 (4)
H(2)	1796 (3)	5407 (3)	2440 (1)	220 (5)	174 (4)	143 (4)	-15 (4)	29 (4)	-44 (4)
		g_{11}	5.3 (2)		g_{12}	-40 (7)			
		g_{22}	50 (16)		g_{13}	8 (5)			
		g_{33}	284 (27)		g_{23}	-84 (25)			

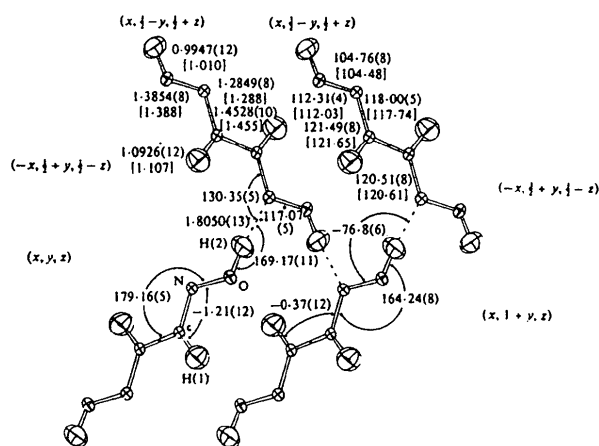


Fig. 1. Atomic notation, thermal ellipsoids (75% probability), and dimensions (Å and deg) in the hydrogen-bonded layers of the crystal structure of glyoxime.

The thermal-motion analysis

The thermal motion of the molecule was analyzed using the segmented-body method, *ORSBA* (Johnson, 1970). An initial calculation was made to obtain an estimate of the non-torsional internal motion of the hydrogen atoms, which were then subtracted out before fitting the segmented-body model. The five atoms of the asymmetric unit were grouped into two segments, CNO, and each hydrogen by itself, excluding the other hydrogen from the refinement. One flexible joint interconnected the two segments and another flexible joint interconnected the parent segment (CNO) with the stationary lattice. For the methylene hydrogen, the C—H r.m.s. stretch correction was 0.080 Å, the in-plane bending was 0.113 Å and the out-of-plane bending was 0.066 Å. For the hydroxyl hydrogen, a r.m.s. stretch of 0.069 Å, in-plane bending of 0.102 Å, and out-of-plane bending of 0.102 Å were assumed (Cyvin, 1968).

The segmented model used for the rigid-body analysis had one segment (CHNOH) with a flexible joint from the center of symmetry to the stationary lattice. This is equivalent to a standard Schomaker & Trueblood (1968) rigid-body analysis. With the hydrogen vibrational motion subtracted, the overall fit was good [$\langle r.m.s. U_{ij} - U_{ijSMB} \rangle = 0.0004 \text{ \AA}^2$ and $\sigma(U_{ij}) = 0.0005 \text{ \AA}^2$]. The rigid-body motion of the molecule with respect to **a**, **b**, and **c*** is:

		a	b	c*
T	0.072 Å	20.2°	70.5°	95.1°
	0.065	89.2	77.1	12.9
	0.055	69.8	156.4	78.2
ω	5.9°	75.0	48.4	45.5
	1.2	127.4	116.9	49.3
	1.0	41.3	126.5	73.4.

The thermal-motion bond-length corrections of ~0.003 Å were similar to those calculated for the other low-temperature neutron diffraction studies in this series of investigations. As in these previous studies, comparison with theory suggests that the thermal-motion corrections in the C—H and O—H bond lengths, based on internal vibrational motion and rigid-body motion, are over-estimated, due to neglect of the compensatory nature of the anharmonic motion. For these bonds, a more realistic comparison with theory is obtained if it is assumed that these two effects cancel at temperatures close to 0 K.

Discussion of the structure

The crystal structure is as determined by Calleri, Ferraris & Viterbo (1966). The differences in the atomic coordinates for the non-hydrogen atoms did not

Table 3. *Experimental and theoretical molecular dimensions of glyoxime at 9 K*

	Experimental		Theoretical HF/3-21G	
	Observed	Corrected		
Bond lengths (Å)				
C—C'	1.4528 (10)	1.455	1.463	
C=N	1.2849 (8)	1.288	1.258	
N—O	1.3854 (8)	1.388	1.439	
C—H(1)	1.0926 (12)	1.107	1.072	
O—H(2)	0.9947 (12)	1.010	0.967	
Bond angles (°)				
C'—C—N	118.00 (5)	117.74	118.9	
C—N—O	112.31 (4)	112.03	110.3	
C'—C—H(1)	120.51 (8)	120.61	118.5	
N—C—H(1)	121.49 (8)	121.65	122.6	
N—O—H(2)	104.76 (8)	104.48	103.9	
Torsion angles (°)				
N'—C'—C—H(1)	0.37 (12)		100	
C'—C—N—O	179.16 (4)		180	
O—N—C—H(1)	-1.21 (13)		0	
C—N—O—H(2)	164.24 (8)		180	
Hydrogen-bond lengths (Å) and angle (°)				
H(2)···N	1.8050 (13)			
O···N	2.7883 (12)			
O—H(2)···N	169.17 (11)			
Deviations from planarity ($Ax + By + Cz - D = 0$)				
	A	B	C	D
(i)	2.737	-2.708	2.863	-0.011
(ii)	-2.726	2.715	-2.900	0.009
	(i)		(ii)	
C	0.0027 (5)	0		
N	-0.0013 (3)	0		
O	0.0016 (5)	0		
H(1)	-0.0120 (13)	[0.0195]*		
H(2)	[-0.2630 (12)]*	[0.2614]*		

* Not included in the weighted least-squares plane.

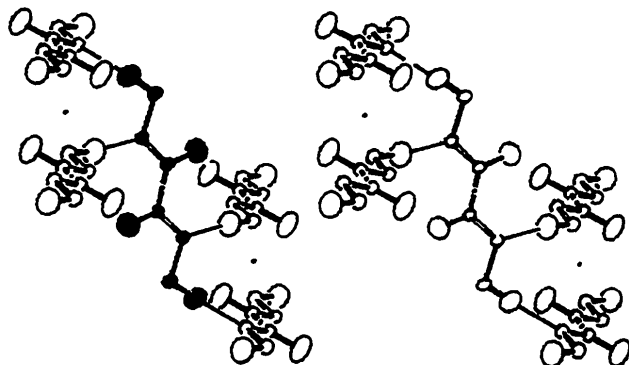
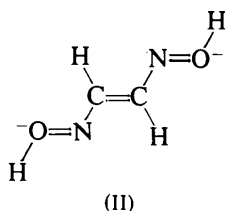


Fig. 2. Stereoview of the orientation of adjacent hydrogen-bonded layers in the crystal structure of glyoxime, viewed along a normal to the plane of one of the molecules.

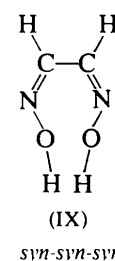
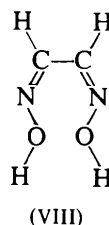
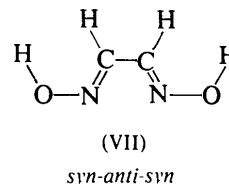
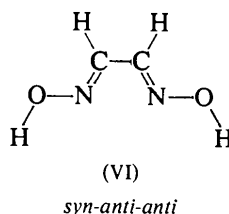
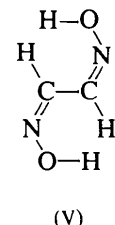
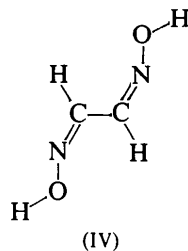
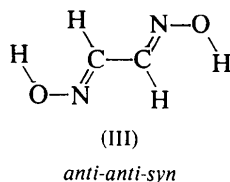
exceed 0.05 Å. The molecular dimensions and the hydrogen-bond data are given in Table 3 and Fig. 1. The molecule is very close to being planar, except for the O—H bond, which is oriented 15.8° out of the plane. This corresponds to a displacement of the hydrogen atom from the least-squares plane of the non-hydrogen atoms of 0.263 (1) Å.

The molecules have the *anti-anti-anti* conformation (I), with dimensions which are consistent with the major valence-bond resonance representations of (I), with a minor contribution from (II). In the crystal, the molecules are hydrogen bonded into buckled layers, parallel to (100), which accounts for the marked cleavage along that direction (and probably the anisotropic extinction). The separation between these layers is the *a* translation, 3.745 (1) Å, corresponding to van der Waals interactions between the hydrogen-bonded layers. As shown in the stereoview in Fig. 2, the adjacent rows of hydrogen-bonded glyoxime molecules in the same layer are oriented with their planes at nearly 90° to each other.



The *ab-initio* molecular-orbital calculations

There are four planar conformations of glyoxime with symmetry C_i , (I,III,IV,V), four with symmetry C_{2v} , (VI,VII,VIII,IX), and an infinite number with lower symmetries.



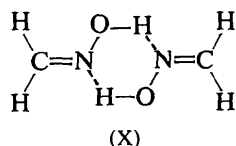
Of these, I, IV, and VI are candidates for minimum-energy conformations. Their energies, calculated at HF/STO-3G level, are given in Table 4. These, and all higher-level approximations including the geometry optimizations, were carried out using *GAUSSIAN 80* (Binkley, Whiteside, Krishnan, Seeger, DeFrees, Schlegel, Topiol, Kahn & Pople, 1980). As anticipated, I, the conformer in the crystal structure, is the minimum-energy conformation. However, the predicted energy differences between I, IV, and VI are relatively small, indicating that rotation about the N—O and C—C bonds will occur in the gas phase, and possibly in solution also. The optimum geometry for I was then calculated at the HF level with a 3-21G basis set, giving the results shown in Table 3.

Table 4. Theoretical energies for related planar conformers of glyoxime, calculated at the HF/STO-3G level, with optimized geometry

Conformer	Hartrees*	kJ mol ⁻¹	kcal mol ⁻¹
(I) <i>anti-anti-anti</i>	332.17934	0.0	(0.0)
(IV) <i>anti-syn-anti</i>	332.17663	7.39	(1.7)
(VI) <i>syn-anti-anti</i>	332.17575	9.78	(2.2)

* 1 hartree = 4.35916 × 10¹⁸ J.

To provide information concerning the effect of the hydrogen bonding on the $C=N-O-H$ bond lengths, the geometry of a model of the hydrogen-bonded dimer of a simpler analogue, formaldehyde oxime (X) was optimized at the HF/STO-3G level and compared with the optimized geometry of the monomer at the same level of approximation. The results of this calculation are shown in Fig. 3. The calculated $O-H\cdots N$ hydrogen-bond length of 1.911 Å is less than that calculated for the $N-H\cdots O=C$ bond in the formamide oxime dimer (1.822 Å, Jeffrey *et al.*, 1981b), and the effect of hydrogen-bond dimerization on the dimensions of the isolated molecule is smaller than was calculated for formamide. In that calculation, $C=O$ and $C-N$ distances changed by +0.018 and -0.023 Å in going from monomer to dimer. In the formaldehyde oxime, only the $N-O$ and $O-H$ bond lengths are significantly changed. The calculated hydrogen bond is 0.1 Å longer than that observed in the crystal structure. This difference is not unexpected in view of the disparity between the dimer model and actual crystal structure and the level of theoretical approximation. HF/STO-3G calculations provide reliable comparisons between like systems, but do not provide good absolute geometries or energies.



As in the previous studies in this series, the differences between the theoretical and experimental bond lengths are corrected for approximations in the theory by extrapolation from calculations on simpler molecules and for hydrogen bonding using the formaldehyde oxime dimer model. These results are shown in Table

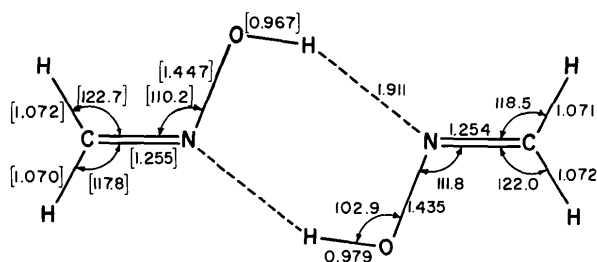


Fig. 3. Geometry of the hydrogen-bonded formaldehyde oxime dimer optimized at the HF/STO-3G level. Values in square brackets are for the monomer at HF/STO-3G. (Distances in Å, angles in degrees.)

5. The residual discrepancies are very close to those obtained in the analogous study of formamide oxime (Jeffrey *et al.*, 1981b). In that work, initial discrepancies of -0.030 and +0.034 Å between the theoretical and experimental $C=N$ and $N-O$ bond lengths were reduced to -0.011 and +0.015 Å, when the same type of corrections was applied.

In both analyses, better agreement between theory and experiment is obtained for the $C-H$ and $O-H$ bond lengths if the thermal-motion corrections are omitted. As noted previously (Jeffrey *et al.*, 1982), we believe this is due to the compensation of thermal shortening and anharmonic lengthening of $X-H$ bonds in these types of crystals at temperatures around 10 K.

As we have noted in the earlier studies, excellent agreement is obtained for bonds between like atoms, $C-C$ and $N-N$, with discrepancies of less than 0.005 Å. Good agreement, <0.005 Å, was also obtained for the $C-F$ bond in monofluoroacetamide. For multiple bonds, $C=O$ and $C=N$, the theoretical values are shorter than the corrected observed values by 0.005 to 0.015 Å. For the bonds between the electro-

Table 5. Analysis of bond-length discrepancies (Å)

Values in parentheses are uncorrected for riding motion.

Bond	Theory - experiment	Higher level extrapolation MP3/6-31G*	H-bonding dimer - monomer [¶]	Residual discrepancy
C-C	+0.008	-0.016†		-0.008
C=N	-0.030	+0.019‡	-0.001	-0.012
N-O	+0.051	-0.025§	-0.012	+0.014
C-H	-0.035	+0.021		-0.014
	(-0.020)			(+0.001)
O-H	-0.053	+0.001≠	+0.012	-0.040
	(-0.028)			(-0.015)

† From ethane (MP2/6-31G*).

‡ From methyleneamine.

§ From hydroxylamine.

|| From formaldehyde.

≠ From methanol.

¶ From formaldehyde oxime dimer at HF/3-21G.

negative atoms, N—O, the calculated values are 0.010 to 0.015 Å longer than the experimental values.

We ascribe these significant differences in agreement between theory and experiment to the effect of electron correlation in high-electron-density bonds, which is not accounted for adequately by extrapolation from higher-level calculations on simpler molecules, rather than to crystal-field effects.

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Structure of 6-{2-(3-Ethyl-2,3-dihydro-1,3-benzothiazol-2-ylidene)ethylidene}-2-methoxy-4-nitro-2,4-cyclohexadienone: A Model Compound for a Photomerocyanine

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Abstract

$C_{18}H_{16}N_2O_4S$ is monoclinic, space group $P2_1/c$, with $a = 13.019$ (9), $b = 7.696$ (8), $c = 16.471$ (10) Å, $\beta = 91.95$ (5)°, $V = 1649.3$ Å³, $D_c = 1.44$ Mg m⁻³, $Z = 4$, $\mu(\text{Mo } K\alpha) = 0.225$ mm⁻¹. The crystal structure has been determined from Mo $K\alpha$ data and refined to an R value of 0.062 for 1701 observed reflexions. In the solid state the polar zwitterionic form of the merocyanine is dominant. The molecular geometry of the thiazole ring approaches that of a thiazolium cation

and the phenolate ring is the negatively charged moiety of the molecule. In the crystal lattice the molecules associate in pairs across centres of inversion. The slip angle is 55°.

Introduction

Colorless photochromic spiropyran compounds (A) transform, by the action of ultraviolet light, into strongly colored compounds. The structure of these colored forms was assigned on the basis of the