The support of LJF by PPG Industries is gratefully acknowledged. We thank a referee for helpful comments. Partial support of this research through the purchase of the diffractometer system by an NIH grant is also gratefully acknowledged.

References

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Gerkin, R. E., Lundstedt, A. P. & Reppart, W. J. (1984). *Acta Cryst.* C**40**, 1892–1894.

Gerkin, R. E. & Reppart, W. J. (1986). *Acta Cryst.* C**42**, 480–482.

Gilman, H., Tolman, L., Yeoman, F., Woods, L. A., Shirley, D. A. & Avakian, S. (1946). *J. Am. Chem. Soc.* **68**, 426–428.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42–46.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1989). *TEXSAN. TEXRAY Structure Analysis Package*, Version 5.0. MSC, 3200A Research Forest Drive, The Woodlands, TX 77381, USA.

Reppart, W. J., Gallucci, J. C., Lundstedt, A. P. & Gerkin, R. E. (1984). *Acta Cryst.* C**40**, 1572–1576.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3174–3187.

Still, W. C., Kahn, M. & Mitra, A. (1978). *J. Org. Chem.* **43**, 2923–2925.

Acta Cryst. (1991). C**47**, 2137–2141

Structures of Photochromic Spiroindolinobenzoxazines and a Spiroindolinobenzopyran

By Yasuko T. Osano, Kazuo Mitsuhashi, Shuichi Maeda and Takao Matsuzaki

Research Center, Mitsubishi Kasei Corporation, Kamoshida, Midoriku, Yokohama 227, *Japan*

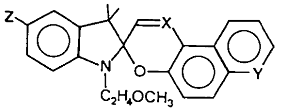
(*Received* 22 *November* 1990; *accepted* 18 *March* 1991)

Abstract. The crystal structures of two photochromic spirooxazines and a related spiropyran have been determined by X-ray crystallographic techniques. Crystal data are: 1-(2-methoxyethyl)-3,3,5-trimethylspiro[indoline-2,2′-[2*H*]-naphtho[2,1-*b*][1,4]oxazine] (1), $C_{25}H_{26}N_2O_2$, $M_r = 386·5$, orthorhombic, $P2_12_12_1$, $a = 10·913\ (3)$, $b = 18·603\ (4)$, $c = 10·231\ (3)$ Å, $V = 2077$ Å^3, $Z = 4$, D_m (flotation) $= 1·25$, $D_x = 1·236$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 5·85$ cm^{-1}, $F(000) = 824$, $T = 296$ K, $R = 0·064$ for 2040 reflections with $|F| \geq \sigma(|F|)$; 1-(2-methoxyethyl)-3,3-dimethylspiro[indoline-2,2′-[2*H*]-pyrido[3,2-*f*][1,4]-benzoxazine] (2), $C_{23}H_{23}N_3O_2$, $M_r = 373·5$, monoclinic, $P2_1/c$, $a = 22·029\ (2)$, $b = 10·885\ (1)$, $c = 17·549\ (1)$ Å, $\beta = 96·27\ (1)°$, $V = 4182·8$ Å^3, $Z = 8$, D_m (flotation) $= 1·26$, $D_x = 1·186$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 5·80$ cm^{-1}, $F(000) = 1584$, $T = 296$ K, $R = 0·065$ for 7001 reflections with $|F| \geq \sigma(|F|)$; 1-(2-methoxyethyl)-3,3,5-trimethylspiro[indoline-2,2′-[2*H*]-naphtho[2,1-*b*]pyran] (3), $C_{26}H_{27}NO_2$, $M_r = 385·5$, monoclinic, $P2_1/c$, $a = 19·271\ (1)$, $b = 6·764\ (1)$, $c = 16·302\ (3)$ Å, $\beta = 96·27\ (1)°$, $V = 2112·2$ Å^3, $Z = 4$, D_m (flotation) $= 1·18$, $D_x = 1·213$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·5418$ Å, $\mu = 5·60$ cm^{-1}, $F(000) = 824$, $T = 296$ K, $R = 0·072$ for 4035 reflections with $|F| \geq \sigma(|F|)$. The distances of the $C_{\rm spiro}$—O bond which cleaves on photoreaction are similar in the three compounds but the $C_{\rm spiro}$—N bond distance in the spiropyran is longer than those in the spirooxazines. The spiropyran also has the strongest intramolecular short contacts compared with spirooxazines. These structural differences suggest that an unstable photoproduct is the reason why the spiropyran shows photochromism only at low temperatures.

Introduction. While photochromic spiroindolinobenzopyrans have been extensively studied (Tyer & Becker, 1970*a*,*b*; Aldoshin, Atovmyan, D'yachenko & Gal'bershtam, 1981; Aldoshin & Atovmyan, 1984, 1987; Aldoshin, Atovmyan & Kozina, 1986, 1987*a*,*b*) only a few spectral and structural studies (Chu, 1983; Clegg, Norman, Lasch & Kwak, 1987; Clegg, Norman, Flood, Sallans, Kwak, Kwiatkowski & Lasch, 1991) have been reported for spiroindolinobenzoxazines. Spirooxazines are useful compounds because they show greater durability than spiropyrans on repeated photochromic reactions. Structural information seems to be important for understanding the photochromic properties and mechanisms of the photocolouration. The present paper describes the crystal structures of spiroindolinobenzoxazines, (1) and (2), and a related spiroindolinobenzopyran (3). (1) and (3) have similar

0108-2701/91/102137-05$03.00

chemical structures except that (3) has a =CH— group in place of =N— in (1), which makes (3) a spiropyran compound (see below). However, they show considerably different behaviour for photochromism. (1) and (2) show photocolouration at room temperature in solution upon UV irradiation. (3), on the other hand, shows photocolouration only when it is cooled down to 253 K. The structural features, such as the C_{spiro}—O bond distance, intramolecular short contacts and ring planarity, which are related to the difference in photochromic behaviour, will be discussed.



(1) $X = N$, $Y = CH$, $Z = CH_3$
(2) $X = N$, $Y = N$, $Z = H$
(3) $X = CH$, $Y = CH$, $Z = CH_3$

Experimental. The synthesis of (1), (2) and (3) will be described elsewhere (S. Maeda, private communication). Crystals suitable for X-ray analysis were obtained by recrystallization from a methanol solution. Experimental details are summarized in Table 1. The structure of (2) contains two crystallographically independent molecules, which will be named (2*A*) and (2*B*) hereafter. Scattering factors were those embedded in *SHELX*76.

Discussion. The final atomic coordinates for the non-hydrogen atoms are given in Tables 2, 3 and 4.* Selected bond distances and angles are summarized in Table 5.

The distances of the C_{spiro}—O bond, which cleaves upon photoexcitation, show no significant differences in these three compounds [(1) 1·463 (5), (2*A*) 1·458 (3), (2*B*) 1·462 (3), (3) 1·464 (2) Å], and are longer than the values found in oxygen-containing heterocycles (1·41–1·43 Å) (*Molecular Structures and Dimensions*, 1972) but are shorter than those in the 6′-nitroindolinospirobenzopyrans (1·471–1·500 Å) (Aldoshin, Atovmyan, D'yachenko & Gal'bershtam, 1981; Aldoshin & Atovmyan, 1984, 1987; Aldoshin, Atovmyan & Kozina, 1986, 1987*a*,*b*). The C_{spiro}—N bond distances, however, show notable differences. The spirooxazine molecules, (1), (2*A*) and (2*B*), have similar distances [(1) 1·425 (6), (2*A*) 1·434 (3), (2*B*) 1·427 (2) Å] while in (3) the bond distance is 1·459 (2) Å. The longer C_{spiro}—N bond distance seems to be unfavourable for photocolouration, because in the stable photoproduct the C—N bond must have double-bond character due to the resonance of the quinoid form and, consequently, the bond length becomes shorter.

Table 1. *Experimental details*

	(1)	(2)	(3)
Crystal dimensions (mm)	0·3 × 0·3 × 0·1	0·7 × 0·5 × 0·2	0·4 × 0·3 × 0·2
No. and range of reflections for lattice-parameter refinement	12 $36 < 2\theta < 46°$	21 $40 < 2\theta < 52°$	12 $40 < 2\theta < 60°$
Diffractometer		Enraf–Nonius CAD-4	
Scan mode	ω–0·3θ	ω–1·3θ	ω–0·3θ
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0·625	0·625	0·625
No. of standard reflections		3 after every 1·5 h	
Empirical absorption correction (max. and min. correction factor)	Not applied	Applied (0·9998, 0·809)	Not applied
h	0→13	−27→27	0→24
k	0→23	0→13	0→8
l	0→12	0→21	−20→20
No. of unique reflections measured	2470	8371	4192
No. of reflections used $\lvert F_o\rvert \geq \sigma(\lvert F_o\rvert)$	2040	7001	4035
Structure determination	*SHELXS*86 (Sheldrick, 1986)	*MULTAN*78 (Main *et al.*, 1978)	
Refinement		*SHELX*76 (Sheldrick, 1976)	
Residual density (e Å^{-3})	0·2	0·2	0·3
$(\Delta/\sigma)_{max}$	0·08	0·14	0·06
Function minimized		$w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	
Weight	$0{\cdot}731/[\sigma^2(F) - 0{\cdot}002F^2]$	$[\sigma^2(F) - 0{\cdot}013F^2]^{-1}$	$[\sigma^2(F) - 0{\cdot}013F^2]^{-1}$
R, *wR*	0·064, 0·072	0·065, 0·088	0·072,* 0·103
S	1·170	0·836	0·587

* Residual factors *R* and *wR* for 3668 reflections with $\lvert F_o\rvert \geq 3\sigma(\lvert F_o\rvert)$ were 0·066 and 0·086, respectively.

Table 2. *Final atomic coordinates for the non-hydrogen atoms of* (1) (Å^2 × 10^4)

$$B_{eq} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	B_{eq}
C1	10084 (5)	500 (3)	−1020 (5)	5·8
C2	9151 (5)	169 (3)	−1685 (5)	6·0
C3	7935 (5)	268 (3)	−1303 (5)	6·0
C4	7639 (4)	695 (2)	−251 (4)	5·4
C5	8576 (4)	1036 (2)	465 (4)	4·6
C6	9814 (4)	956 (2)	57 (4)	4·8
C7	10743 (4)	1324 (3)	754 (4)	5·3
C8	10478 (4)	1755 (3)	1796 (5)	5·2
C9	9253 (4)	1827 (3)	2211 (4)	4·9
C10	8317 (4)	1479 (2)	1576 (4)	4·8
N11	7080 (3)	1595 (2)	1943 (4)	5·6
C12	6896 (4)	1954 (3)	2965 (4)	5·7
C13	7841 (4)	2260 (3)	3886 (4)	5·2
O14	9037 (3)	2274 (2)	3242 (3)	5·2
N15	7562 (3)	2983 (2)	4239 (3)	5·1
C16	8000 (4)	3113 (2)	5511 (4)	4·9
C17	8257 (4)	2480 (2)	6123 (4)	4·7
C18	7970 (4)	1865 (2)	5221 (4)	4·9
C19	8128 (4)	3768 (2)	6149 (4)	5·3
C20	8521 (4)	3753 (3)	7440 (5)	5·5
C21	8769 (4)	3110 (3)	8076 (4)	5·0
C22	8648 (4)	2470 (3)	7410 (4)	5·0
C23	7426 (4)	3549 (3)	3275 (4)	5·5
C24	8608 (4)	3905 (3)	2871 (5)	6·0
O25	8299 (3)	4491 (2)	2049 (4)	7·4
C26	9355 (6)	4885 (3)	1676 (7)	8·0
C27	6726 (5)	1539 (3)	5644 (6)	6·4
C28	8935 (5)	1269 (3)	5208 (5)	6·0
C29	9207 (5)	3115 (3)	9513 (4)	6·7

The molecules (1), (2*A*), (2*B*) and (3) are very crowded around the spiro-carbon atoms. The intramolecular short contacts are given in Table 6. There are a number of short contacts around the oxygen

---

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54101 (60 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Final atomic coordinates for the non-hydrogen atoms of* (2) (Å$^2 \times 10^4$)

$B_{cq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
N1*A*	7190 (1)	−925 (2)	5342 (1)	5·2
C2*A*	7402 (1)	5 (3)	5027 (2)	5·5
C3*A*	7283 (1)	1241 (3)	5138 (2)	5·1
C4*A*	6910 (1)	1539 (2)	5592 (1)	4·3
C5*A*	6668 (1)	579 (2)	5940 (1)	3·7
C6*A*	6828 (1)	−647 (2)	5809 (1)	4·1
C7*A*	6602 (1)	−1621 (2)	6168 (2)	4·7
C8*A*	6241 (1)	−1403 (2)	6645 (1)	4·3
C9*A*	6074 (1)	−192 (2)	6763 (1)	3·5
C10*A*	6274 (1)	785 (2)	6417 (1)	3·5
N11*A*	6128 (1)	2003 (2)	6563 (1)	4·3
C12*A*	5746 (1)	2146 (2)	6949 (1)	4·5
C13*A*	5410 (1)	1148 (2)	7255 (1)	3·9
O14*A*	5725 (1)	−32 (1)	7259 (1)	4·0
N15*A*	5459 (1)	1407 (2)	8076 (1)	4·2
C16*A*	4909 (1)	966 (2)	8202 (1)	4·1
C17*A*	4424 (1)	713 (2)	7462 (1)	4·1
C18*A*	4661 (1)	1017 (2)	6777 (1)	4·1
C19*A*	4799 (1)	820 (3)	8928 (2)	5·5
C20*A*	4191 (2)	432 (3)	8893 (2)	6·2
C21*A*	3711 (1)	193 (3)	8163 (2)	6·1
C22*A*	3815 (1)	326 (2)	7433 (2)	5·2
C23*A*	6078 (1)	1553 (2)	8732 (2)	4·8
C24*A*	6432 (1)	373 (2)	9082 (2)	5·1
O25*A*	6912 (1)	660 (2)	9829 (1)	7·0
C26*A*	7338 (2)	−313 (4)	10177 (2)	7·9
C27*A*	4364 (1)	2253 (3)	6398 (2)	5·6
C28*A*	4507 (1)	33 (3)	6114 (2)	5·8
N1*B*	7960 (1)	1237 (2)	3387 (1)	5·2
C2*B*	7605 (1)	2136 (3)	2951 (2)	5·6
C3*B*	7691 (1)	3375 (3)	3162 (2)	5·4
C4*B*	8169 (1)	3719 (2)	3871 (1)	4·4
C5*B*	8561 (1)	2794 (2)	4366 (1)	3·7
C6*B*	8446 (1)	1556 (2)	4100 (1)	4·0
C7*B*	8841 (1)	625 (2)	4574 (1)	4·2
C8*B*	9324 (1)	880 (2)	5303 (1)	4·1
C9*B*	9419 (1)	2097 (2)	5579 (1)	3·7
C10*B*	9067 (1)	3045 (2)	5117 (1)	3·8
N11*B*	9228 (1)	4278 (2)	5337 (1)	4·6
C12*B*	9621 (1)	4460 (2)	6062 (1)	4·8
C13*B*	9882 (1)	3496 (2)	6704 (1)	4·0
O14*B*	9902 (1)	2315 (1)	6317 (1)	4·1
N15*B*	10529 (1)	3761 (2)	7231 (1)	4·3
C16*B*	10635 (1)	3329 (2)	8015 (1)	4·2
C17*B*	10045 (1)	3066 (2)	8096 (1)	4·1
C18*B*	9499 (1)	3382 (2)	7314 (1)	4·2
C19*B*	11214 (1)	3179 (3)	8657 (1)	5·1
C20*B*	11184 (2)	2741 (3)	9389 (1)	5·8
C21*B*	10604 (2)	2485 (3)	9478 (2)	5·8
C22*B*	10018 (1)	2658 (2)	8819 (2)	5·0
C23*B*	11050 (1)	3969 (2)	6924 (2)	4·9
C24*B*	11416 (1)	2828 (3)	6854 (2)	5·4
O25*B*	11939 (1)	3192 (2)	6629 (2)	7·6
C26*B*	12385 (1)	2272 (3)	6673 (2)	6·8
C27*B*	9217 (1)	4649 (3)	7418 (2)	5·8
C28*B*	8959 (1)	2417 (3)	7053 (2)	5·9

atoms in the cleaving bonds, and the shortest distances around the oxygen atom are observed in (3).

The *ORTEP* drawings are shown in Figs. 1, 2 and 3. The spirooxazines (1), (2*A*) and (2*B*) and the spiropyran (3) assume apparently different conformations. The difference mainly arises from the conformational change in the oxazine and pyran rings. The oxazine rings of (1) and (2) are bent towards the *gem*-methyl group, while the pyran ring of (3) is bent in the opposite direction. The oxazine rings in (1), (2*A*) and (2*B*) have similar torsion angles (Table 7). The pyran ring in (3), on the other hand, has different torsion angles (by 30–50°) with opposite signs compared with the corresponding torsion angles in the spirooxazines.

Table 4. *Final atomic coordinates for the non-hydrogen atoms of* (3) (Å$^2 \times 10^4$)

$B_{eq} = (4/3)\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
C1	5428 (1)	1330 (4)	9167 (1)	5·4
C2	5024 (1)	2968 (4)	9219 (2)	6·1
C3	5048 (1)	4492 (4)	8649 (2)	5·9
C4	5474 (1)	4371 (3)	8023 (1)	5·0
C5	5901 (1)	2693 (3)	7948 (1)	4·0
C6	5871 (1)	1133 (3)	8528 (1)	4·3
C7	6293 (1)	−560 (3)	8474 (1)	4·7
C8	6739 (1)	−717 (3)	7889 (1)	4·5
C9	6771 (1)	839 (2)	7313 (1)	3·9
C10	6353 (1)	2495 (3)	7315 (1)	4·0
C11	6389 (1)	3901 (3)	6642 (1)	4·8
C12	6871 (1)	3718 (3)	6121 (1)	4·8
C13	7430 (1)	2186 (3)	6226 (1)	4·0
O14	7222 (1)	553 (2)	6735 (1)	4·4
N15	8090 (1)	3015 (2)	6595 (1)	4·0
C16	8629 (1)	1785 (3)	6388 (1)	3·8
C17	8382 (1)	554 (3)	5734 (1)	4·1
C18	7645 (1)	1164 (3)	5427 (1)	4·5
C19	9314 (1)	1686 (3)	6738 (1)	4·6
C20	9744 (1)	238 (3)	6442 (1)	5·0
C21	9496 (1)	−1077 (3)	5825 (1)	5·1
C22	8812 (1)	−868 (3)	5462 (1)	4·9
C23	8131 (1)	3953 (3)	7402 (1)	4·2
C24	8381 (1)	6055 (2)	7391 (1)	4·0
O25	8399 (1)	6760 (2)	8207 (1)	4·7
C26	8655 (1)	8711 (3)	8299 (1)	5·7
C27	7688 (1)	2682 (4)	4733 (1)	6·1
C28	7162 (1)	−523 (4)	5123 (2)	6·8
C29	9969 (2)	−2695 (4)	5567 (2)	7·3

Table 5. *Selected bond distances* (Å) *and angles* (°)

	(1)	(2*A*)	(2*B*)	(3)
C9—C10	1·373 (6)	1·373 (3)	1·371 (3)	1·379 (2)
C9—O14	1·364 (5)	1·361 (3)	1·373 (2)	1·363 (2)
C10—*X*11	1·418 (5)	1·409 (3)	1·406 (3)	1·459 (2)
*X*11—C12	1·257 (6)	1·263 (4)	1·274 (3)	1·332 (3)
C12—C13	1·509 (6)	1·516 (3)	1·498 (3)	1·490 (3)
C13—O14	1·463 (5)	1·458 (3)	1·462 (3)	1·464 (2)
C13—N15	1·425 (6)	1·434 (3)	1·427 (2)	1·459 (2)
C13—C18	1·557 (6)	1·568 (3)	1·584 (4)	1·569 (2)
N15—C16	1·407 (5)	1·394 (3)	1·393 (3)	1·401 (2)
N15—C23	1·451 (5)	1·448 (2)	1·448 (4)	1·455 (2)
C16—C17	1·363 (6)	1·385 (3)	1·386 (4)	1·395 (2)
C17—C18	1·503 (6)	1·507 (4)	1·509 (3)	1·511 (2)
C18—C27	1·550 (6)	1·540 (3)	1·549 (4)	1·537 (3)
C18—C28	1·529 (6)	1·530 (4)	1·530 (4)	1·521 (3)
C10—C9—O14	121·6 (4)	121·7 (2)	120·9 (2)	122·2 (1)
C9—C10—*X*11	120·8 (4)	121·3 (2)	121·4 (2)	116·9 (2)
C10—*X*11—C12	117·0 (4)	116·8 (2)	116·0 (2)	120·8 (2)
*X*11—C12—C13	127·7 (4)	127·1 (2)	125·8 (2)	122·5 (2)
C12—C13—O14	109·6 (3)	109·9 (2)	109·4 (2)	110·5 (1)
C12—C13—N15	111·6 (4)	110·0 (2)	111·9 (2)	111·5 (2)
C12—C13—C18	115·6 (4)	115·4 (2)	114·2 (2)	117·7 (1)
O14—C13—N15	106·7 (3)	107·6 (2)	106·9 (2)	109·6 (1)
O14—C13—C18	108·8 (3)	109·3 (2)	110·9 (2)	104·6 (1)
N15—C13—C18	104·1 (3)	104·2 (2)	103·2 (2)	102·3 (1)
C13—O14—C9	119·5 (3)	119·1 (2)	116·8 (1)	121·3 (1)
C13—N15—C16	108·9 (4)	109·4 (2)	110·4 (2)	108·0 (1)
C13—N15—C23	122·3 (4)	122·4 (2)	122·2 (2)	120·0 (1)
C16—N15—C23	122·6 (4)	122·5 (2)	122·9 (2)	120·5 (1)
N15—C16—C17	110·3 (4)	110·1 (2)	109·7 (2)	109·8 (2)
C16—C17—C18	109·4 (4)	109·5 (2)	109·5 (2)	108·7 (2)
C13—C18—C17	101·4 (3)	101·0 (2)	100·8 (2)	99·8 (1)
C13—C18—C27	110·5 (4)	110·9 (2)	110·0 (2)	110·9 (2)
C13—C18—C28	113·4 (4)	112·2 (2)	113·3 (2)	113·2 (2)
C17—C18—C27	108·0 (4)	108·8 (2)	108·6 (2)	107·5 (2)
C17—C18—C28	114·4 (4)	114·0 (2)	113·6 (2)	115·0 (2)

The indoline moieties show minor differences. The five-membered heterocycle, *i.e.* the indoline part, assumes a regular envelope form in the spirooxazines (1), (2*A*) and (2*B*). The dihedral angles between the

Table 6. *Intramolecular short contacts* (Å) (*those longer than* 3·2 Å *are not included*)

	(1)	(2*A*)	(2*B*)	(3)
C9···C12	2·697	2·696	2·695	2·772
C10···C13	2·823	2·815	2·770	2·882
*X*11···O14	2·815	2·820	2·812	2·771
C12···C23	3·041	3·020	3·017	3·030
C12···C27	2·854	2·851	2·829	2·977
O14···C16	3·018	3·044	3·048	2·951
O14···C17	3·092	3·118	3·133	2·909
O14···C23	2·953	2·973	2·977	3·021
O14···C24	3·093	3·053	3·176	—
O14···C28	2·748	2·722	2·811	2·718

Table 7. *Selected torsion angles* (°)

	(1)	(2*A*)	(2*B*)	(3)
Oxazine or pyran ring				
C9—O14—C13—N15	−143·1 (4)	−142·5 (2)	−155·2 (2)	−95·7 (2)
C9—O14—C13—C12	−22·1 (5)	−22·8 (2)	−33·8 (2)	27·7 (2)
C9—O14—C13—C18	105·1 (4)	104·9 (2)	92·9 (2)	155·2 (2)
*X*11—C12—C13—O14	17·1 (6)	16·5 (3)	28·3 (3)	−21·8 (2)
*X*11—C12—C13—N15	135·1 (6)	134·9 (3)	146·6 (3)	100·4 (2)
*X*11—C12—C13—C18	−106·3 (6)	−107·6 (3)	−96·6 (3)	−141·8 (2)
C13—O14—C9—C8	−167·5 (5)	−165·8 (2)	−163·3 (2)	165·9 (2)
C13—O14—C9—C10	14·5 (5)	16·4 (2)	19·5 (2)	−16·7 (2)
Indoline ring				
C17—C18—C13—C12	−145·4 (5)	−143·1 (2)	−145·2 (2)	−154·9 (2)
C17—C18—C13—O14	90·8 (4)	92·4 (2)	90·6 (2)	82·1 (2)
C17—C18—C13—N15	−22·7 (4)	−22·4 (2)	−23·5 (2)	−32·2 (2)
C16—N15—C13—C12	149·2 (5)	148·0 (2)	147·7 (2)	157·5 (2)
C16—N15—C13—O14	−91·1 (4)	−92·3 (2)	−92·5 (2)	−79·8 (2)
C16—N15—C13—C18	23·9 (4)	23·8 (2)	24·5 (2)	30·8 (2)
C13—C18—C17—C16	14·4 (4)	14·3 (2)	15·8 (2)	24·1 (2)
C18—C17—C16—N15	−0·5 (6)	−0·6 (2)	−1·9 (2)	−6·4 (2)
C17—C16—N15—C13	−15·6 (4)	−15·4 (2)	−15·2 (2)	−16·3 (2)

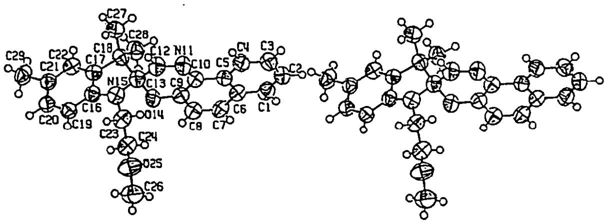
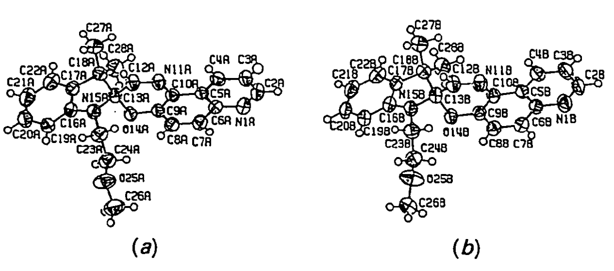


Fig. 1. Molecular structure of (1).



(*a*) (*b*)

Fig. 2. Molecular structure of (*a*) (2*A*) and (*b*) (2*B*).

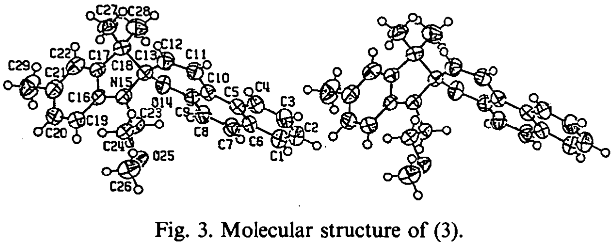
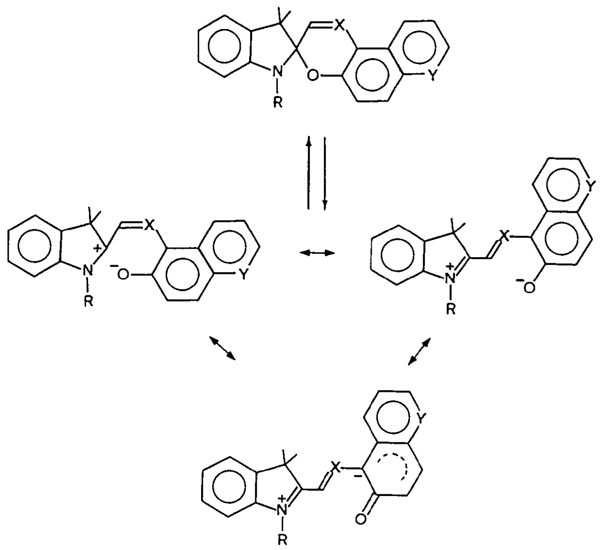


Fig. 3. Molecular structure of (3).

two planes (N15—C16=C17—C18 and N15—C13—C18) are 23·9 (1), 12·7 (2*A*) and 24·5° (2*B*). The heterocycle in the spiropyran (3) has a slightly distorted envelope form with poorer planarity (±0·03 Å) for the N15—C16=C17—C18 plane than the planes in the spirooxazines (±0·01 Å) and with a larger dihedral angle (32·7°).

Photocolouration in the present study is considered to be a two-step reaction (see below). In the first step, a C_{spiro}—O bond cleaves upon photoexcitation, and in the second step, the photoproduct changes its conformation to become a stable species, which can be converted to the starting compound by heating. Thus, important factors for this reaction are (*a*) how easily a C_{spiro}—O bond can be cleaved (photoreactivity) and (*b*) the stability of the photoproducts. The C_{spiro}—O bond distance and the intramolecular short contacts are direct measurements of photoreactivity, since a longer bond distance means weaker bond character and steric repulsion could lead to bond breakage. The C_{spiro}—N bond distance and the planarity of oxazine or pyran, might be related to the stability of photoproducts. The C_{spiro}—N bond is likely to be short and also the planarity is likely to be good in a stable form due to the contribution of a resonant quinoid form.



The structural features of the spirooxazines and the spiropyran revealed in the present study are (*a*) the C_{spiro}—O bond distances are longer than the normal value but similar in three compounds, (*b*) short contacts around the O14 atom are the strongest in the spiropyran (3), (*c*) the C_{spiro}—N bond distance is considerably longer in (3), and (*d*) the degree of planarity in the oxazine or pyran part is poor and roughly equivalent in the three compounds. These observations suggest that the C_{spiro}—O bond in the spiropyran (3) would be the one to break most easily but the product of this compound would also be the most unstable due to the long C_{spiro}—N distances. This interpretation explains the fact that the spiropyran (3) shows photochromism only when cooled down to 253 K, while the spirooxazines (1) and (2) show photocolouration at room temperature. The different photoreaction behaviour of (3) seems to be a result of a ring-closing reaction which is too rapid for the photoproduct to remain in a stable form.

The molecular structures of these compounds could explain the different photochromic behaviour between the spirooxazines and the spiropyran. The accurate molecular and crystal structure given here could be used for theoretical studies which will give further information on the mechanism of photochromism.

References

Aldoshin, S. M. & Atovmyan, L. O. (1984). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 191–194.

Aldoshin, S. M. & Atovmyan, L. O. (1987). *Mol. Cryst. Liq. Cryst.* **149**, 251–290.

Aldoshin, S. M., Atovmyan, L. O., D'yachenko, O. A. & Gal'bershtam, M. A. (1981). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 2720–2729.

Aldoshin, S. M., Atovmyan, L. O. & Kozina, O. A. (1986). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 2593–2595.

Aldoshin, S. M., Atovmyan, L. O. & Kozina, O. A. (1987*a*). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 188–190.

Aldoshin, S. M., Atovmyan, L. O. & Kozina, O. A. (1987*b*). *Izv. Akad. Nauk SSSR Ser. Khim.* pp. 190–192.

Chu, N. Y. C. (1983). *Can. J. Chem.* **61**, 300–305.

Clegg, W., Norman, N. C., Flood, T., Sallans, L., Kwak, W. S., Kwiatkowski, P. L. & Lasch, J. G. (1991). *Acta Cryst.* C**47**, 817–824.

Clegg, W., Norman, N. C., Lasch, J. G. & Kwak, W. S. (1987). *Acta Cryst.* C**43**, 804–806.

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.

Molecular Structures and Dimensions (1972). Vol. *A*1. Utrecht: A. Oosthoek.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Tyer, N. W. Jr & Becker, R. S. (1970*a*). *J. Am. Chem. Soc.* **92**, 1289–1294.

Tyer, N. W. Jr & Becker, R. S. (1970*b*). *J. Am. Chem. Soc.* **92**, 1295–1302.

Acta Cryst. (1991). C**47**, 2141–2144

Structure of Dipyridinium Decaiodide – an Infinite Chain Structure

By Thomas L. Hendrixson, Marc A. ter Horst and Robert A. Jacobson*

Ames Laboratory, USDOE and Department of Chemistry, Iowa State University, Ames, Iowa 50011, *USA*

(*Received* 9 *February* 1990; *accepted* 22 *March* 1991)

Abstract. $2C_5H_6N^+.I_{10}^{2-}$, M_r = 1429·26, orthorhombic, $Pmc2_1$, a = 17·331 (4), b = 4·5336 (7), c = 17·615 (3) Å, V = 1384·0 (4) Å^3, Z = 2, D_x = 3·42 g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 110·8 cm^{-1}, $F(000)$ = 1232, T = 273 K, final R = 0·048 for 555 unique reflections with $|F_o| \geq 3\sigma(|F_o|)$. The I atoms form two distinct moieties, an I_7^- and an I_3^-. The I_7^- ions form interconnected sheets which are parallel to the *ab* plane. The I_3^- ions form an infinite chain which propagates along the **c** direction.

Introduction. This study was carried out as part of a series of investigations aimed at structurally characterizing materials which exhibit extended solid-state interactions. Of special interest are those species which are present in mixed oxidation states.

Experimental. Crystals of this compound are formed as a side product of the reaction that produced crystals of $(NHC_5H_5)SbI_4$ (Hendrixson, ter Horst & Jacobson, 1990). A black needle-shaped crystal of approximate dimensions 0·35 × 0·15 × 0·15 mm was used for data collection on a Syntex $P2_1$ four-circle diffractometer operated in a fixed-width ω-scan mode. The scan width was 1° and each background was measured for one half of the total scan time. Cell parameters were obtained from a least-squares refinement of 13 reflections in the range $6 \leq 2\theta \leq 13°$. One standard reflection was measured every 75 reflections and showed no significant change during data collection. A total of 1827 reflections in the range $2 \leq 2\theta \leq 50°$ (hkl, $0 \leq h \leq 20$, $0 \leq k \leq 5$, $0 \leq l \leq 20$) were collected, of which 555 were considered observed $[|F_o| \geq 3\sigma(|F_o|)]$. The data were corrected for absorption using an empirical ψ-scan method (T_{min}/T_{max} = 0·180/0·219) as well as for Lorentz–

---

* To whom correspondence should be addressed.

0108-2701/91/102141-04$03.00