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.

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Structure of Dipyridinium Decaiodide – an Infinite Chain Structure

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Abstract. $2C_5H_6N^+.I_{10}^{2-}$, $M_r = 1429{\cdot}26$, orthorhombic, $Pmc2_1$, $a = 17{\cdot}331\,(4)$, $b = 4{\cdot}5336\,(7)$, $c = 17{\cdot}615\,(3)$ Å, $V = 1384{\cdot}0\,(4)$ Å^3, $Z = 2$, $D_x = 3{\cdot}42$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 110{\cdot}8$ cm^{-1}, $F(000) = 1232$, $T = 273$ K, final $R = 0{\cdot}048$ 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 ($T_{min}/T_{max} = 0{\cdot}180/0{\cdot}219$) as well as for Lorentz–

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polarization effects. Accurate cell constants were obtained from 15 reflections in the range $25 \leq 2\theta \leq 35°$.

The systematic absences (*h*0*l*: *l* odd) indicated the presence of a *c* glide plane perpendicular to **b**. Thus, there were three possible space groups: *Pmcm*, *P*2*cm* and *Pmc*2$_1$. The direct-methods program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) failed to give a solution in any of the three possible space groups. A sharpened Patterson map was calculated and the I(6)—I(7) vector was used for a superposition. The Fourier-transform coefficients of the superposition map were calculated and the best locations in the superposition map for all of the possible symmetry elements in the three space groups were determined using a reciprocal-space approach (Hendrixson, 1989). Translations consistent with the *c* glide plane were only found for the mirror plane perpendicular to **a** and the 2$_1$ screw axis parallel to **c**, indicating that the correct space group was *Pmc*2$_1$. The positions of the ends of the shift vector relative to the 2$_1$ screw axis were calculated and used as input to a least-squares refinement.

The positions of the remaining non-H atoms were determined from successive structure-factor and electron-density-map calculations. The initial positional and isotropic thermal parameters were refined using a block-matrix least-squares approach. The positional and anisotropic thermal parameters of the I atoms and the isotropic thermal parameters of the remaining non-H atoms were refined to their final values using a full-matrix least-squares procedure, minimizing the function $(|F_o| - |F_c|)^2$ to a conventional residual index $R = 0{\cdot}048$ and a weighted residual index $wR = 0{\cdot}047$, where $w = 1/^2\sigma(|F_o|)$. $(\Delta/\sigma)_{\max} = 0{\cdot}01$; $(\Delta\rho)_{\min,\max} = -1{\cdot}03$, $2{\cdot}06$ e Å^{-3}. The positions of the H atoms were calculated and not refined. The final positional and averaged isotropic thermal parameters for the I atoms and the isotropic thermal parameters for the remaining non-H atoms are given in Table 1.* Selected distances and angles are given in Table 2.

Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A, p. 71). Programs used were *ABSN* (Karcher, 1981) for absorption correction, *FOUR* (Powell & Jacobson, 1980) for Fourier-map generation and *ALLS* (Lapp & Jacobson, 1978) for least-squares refinement.

Table 1. *Refined atomic coordinates* ($\times 10^4$) *and thermal parameters* (Å$^2 \times 10^3$) *with e.s.d.'s in parentheses*

	x	*y*	*z*	*U**
I(1)	5000	5752 (11)	1785 (8)	43
I(2)	3385 (2)	2600 (8)	1834 (5)	55
I(3)	1887 (2)	366 (8)	1855 (5)	65
I(4)	5000	8590 (15)	3525 (5)	61
I(5)	5000	10637 (18)	5000	77
I(6)	0	6629 (13)	1683 (5)	45
I(7)	0	3854 (14)	3313 (5)	54
I(8)	0	908 (11)	4916 (6)	48
N	1646 (28)	6350 (125)	4591 (33)	105 (22)
C(1)	1918 (28)	7019 (117)	3915 (29)	44 (14)
C(2)	2611 (34)	6402 (130)	3660 (36)	64 (20)
C(3)	3047 (31)	4783 (215)	4239 (45)	94 (20)
C(4)	2775 (32)	3776 (117)	4870 (42)	58 (15)
C(5)	2088 (42)	4791 (185)	5084 (43)	103 (24)

* Thermal parameters for non-I atoms are isotropic as refined; those for the I atoms are averaged isotropic *U*'s defined by: $U_{\rm av} = (U_{11} + U_{22} + U_{33})/3$, $T = \exp[2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table 2. *Selected distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

I(1)—I(2)	3·144 (4)	I(6)—I(7)	3·124 (12)
I(1)—I(4)	3·324 (16)	I(6^{i})—I(8)	3·307 (13)
I(1^{i})—I(5)	3·545 (13)	I(7)—I(8)	3·135 (11)
I(2)—I(3)	2·787 (5)	I(7)—N	3·773 (51)
I(4)—I(5)	2·759 (9)		
I(2)—I(1)—I(2^{ii})	125·8 (2)	I(4)—I(5)—I(1^{i})	172·2 (3)
I(2)—I(1)—I(4)	98·7 (3)	I(6)—I(7)—I(8)	178·3 (3)
I(3)—I(2)—I(1)	174·2 (2)	I(7)—I(8)—I(6^{i})	176·1 (3)
I(1)—I(4)—I(5)	176·9 (3)		

Superscripts refer to positions relative to the reference molecule: (i) $-x, \frac{1}{2}+y, -z$; (ii) $-x, y, z$.

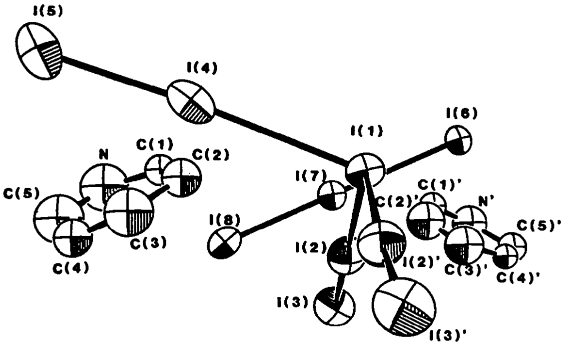

Fig. 1. View showing the structure of $(NHC_5H_5)_2I_{10}$. Thermal ellipsoids are drawn at the 50% probability level.

Discussion. One of the more interesting physical characteristics of this compound is that it forms extremely long needle-shaped crystals, several cm in length. It was initially thought that these crystals were an alternate form of $(NHC_5H_5)SbI_4$. However, the structure, shown in Fig. 1, indicates otherwise.

In $(NHC_5H_5)_2I_{10}$, the I atoms can be separated into two distinct polyiodide moieties, an I_7^- and an I_3^-. The I_7^- ions form interconnected sheets parallel to the *ab* plane, shown in Fig. 2, and the I_3^- ions form an infinite chain which propagates along the **c**

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* 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 54116 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

direction, shown in Fig. 3. The pyridinium ions reside in the regions between the interconnected sheets.

The I_3^- ion is symmetrical, having I(6)—I(7) and I(7)—I(8) distances of 3·135 and 3·124 Å. It has been found that triiodides occurring with large cations are often symmetrical (Mooney, 1938, 1943*a*,*b*), so this result is not unexpected. The distance between the I_3^- ions is 3·307 Å, which is significantly shorter than the van der Waals distances, indicating that there is interaction between neighboring I_3^- ions.

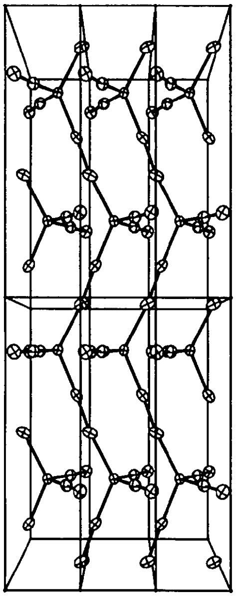

Fig. 2. View of the I_7^- moiety showing the sheets parallel to the *ab* plane. In the figure, the *b* axis is horizontal, the *c* axis is vertical and the *a* axis is perpendicular to the plane of the paper. Thermal ellipsoids are drawn at the 50% probability level.

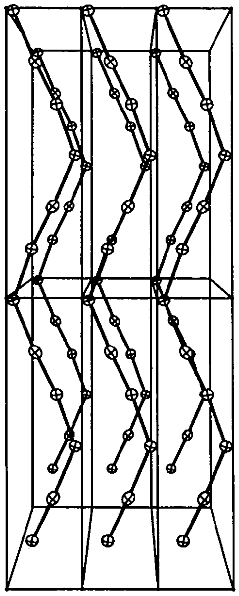

Fig. 3. View of the I_3^- moiety showing the infinite chain in the **c** direction. In the figure, the *b* axis is horizontal, the *c* axis is vertical and the *a* axis is perpendicular to the plane of the paper. Thermal elipsoids are drawn at the 50% probability level.

The I_7^- ions are shaped like distorted trigonal pyramids. They are similar to the I_5^- ions reported previously (Hach & Rundle, 1951; James, Hach, French & Rundle, 1955) in that five of the iodines, I(1), I(2), I(3) and their mirror-related partners, form a *V*-shaped group. These groups form sheets which are parallel to the *ab* plane. The other two iodines, I(4) and I(5), act as bridging iodines, connecting *V*-shaped groups in adjacent sheets. Shorter I(2)—I(3) and I(4)—I(5) distances of 2·787 and 2·759 Å, respectively, along with I(1)—I(2) and I(1)—I(4) distances of 3·144 and 3·324 Å, respectively, are observed. This seems to indicate that the moiety is formed by iodine molecules interacting with an iodide ion, causing partial delocalization of the charge on the iodide ion. The fact that the distance from I(5) to I(1) in the adjacent sheet is 3·545 Å indicates that the I(4)—I(5) dimer is more closely associated with one sheet, justifying the assignment of an I_7^- ion. In the polyiodides previously reported (Hach & Rundle, 1951; James, Hach, French & Rundle, 1955; Havinga, Boswijk & Wiebenga, 1954; Havinga & Wiebenga, 1958), the I—I^- bonds are formed at approximately right angles. While the I(2)—I(1)—I(5) angle is approximately a right angle at 98·7°; the I—I^- bonds in the plane of the sheet form at an angle of 125·8°.

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References

Hach, R. J. & Rundle, R. E. (1951). *J. Am. Chem. Soc.* **73**, 4321–4324.

Havinga, E. E., Boswijk, K. H. & Wiebenga, E. A. (1954). *Acta Cryst.* **7**, 487–490.

Havinga, E. E. & Wiebenga, E. A. (1958). *Acta Cryst.* **11**, 733–737.

Hendrixson, T. L. (1989). PhD dissertation, Iowa State Univ., Ames, USA.

Hendrixson, T. L., ter Horst, M. A. & Jacobson, R. A. (1990). *J. Crystallogr. Spectrosc. Res.* **20**, 107–110.

James, W. J., Hach, R. J., French, D. & Rundle, R. E. (1955). *Acta Cryst.* **8**, 814–818.

Karcher, B. A. (1981). PhD dissertation, Iowa State Univ., Ames, USA.

Lapp, R. L. & Jacobson, R. A. (1978). *ALLS. A Generalized Crystallographic Least-Squares Program.* USDOE Report IS-4708. Iowa State Univ., Ames, USA.

Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Mooney, R. C. L. (1938). *Phys. Rev.* **53**, 851–852.
Mooney, R. C. L. (1943*a*). *Phys. Rev.* **61**, 739–739.
Mooney, R. C. L. (1943*b*). *Phys. Rev.* **64**, 315–315.
Powell, P. R. & Jacobson, R. A. (1980). *FOUR. A Generalized Crystallographic Fourier Program.* USDOE Report IS-4737. Iowa State Univ., Ames, USA.

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Structure de l'Hydroxy-4 (7*H*)-Furo[3,2-*g*][1]benzopyrannone-7 (Bergaptol)

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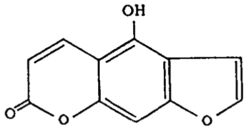
Abstract. $C_{11}H_6O_4$, M_r = 202·2, monoclinic, $P2_1/n$, a = 25·561 (10), b = 3·755 (2), c = 17·704 (7) Å, β = 97·80 (4)°, V = 1683·5 Å^3, Z = 8, D_x = 1·595 Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 1·00 mm^{-1}, F(000) = 832, T = 295 K, $R(F)$ = 0·067 for 3049 reflexions. The two independent molecules are bonded by hydrogen bonds, forming chains approximately parallel to (010) and limited by the (101) plane. Molecules of (I) are stacked among themselves as are the molecules of (II). The stacking distance, nearly the same for both molecules, is 3·39 Å.

Introduction. L'huile de bergamote extraite de l'écorce de *Citrus bergamia* est très utilisée en cosmétologie pour sa remarquable fragrance. Cette huile contient essentiellement des coumarines et furocoumarines, elle peut induire, en présence de rayonnement ultra-violet de grande longueur d'onde (UV-*A*), des altérations cutanées sévères. Ces effets secondaires sont généralement attribués à la présence de 5-MOP (méthoxy-5 psoralène ou méthoxy-5 furo[3,2-*g*]coumarine) dont les propriétés phototoxiques et pigmentogéniques sont bien connues (Parrish, White, Pathak, Fitzpatrick, Eissen, Wolf, Freedberg & Austen, 1979; Marzulli & Mailbach, 1970).

La bergamotine (géranyloxy-5 psoralène) est le 'chromophore' majeur de cette huile et est responsable de 66% de l'absorption UV-*A* et UV-*B*. Une étude actuelle (Martin, Valla, Giraud, Brouard, Morlière, Haigle & Santus, 1991) concernant l'évaluation de la toxicité des photoproduits de la bergamotine a permis de mettre en évidence la production de bergaptol {hydroxy-4 (7*H*)-furo[3,2-*g*][1]benzopyrannone-7} (1), dans la proportion de 30%. Le bergaptol a été recristallisé dans le méthanol et sa détermination structurale entre dans le cadre d'une étude générale des propriétés des photoproduits de la bergamotine et notamment de ses propriétés "d'association" avec d'autres entités présentes dans le milieu réactionnel.



(1)

Partie expérimentale. Cristal incolore, 0,06 × 0,35 × 0,13 mm, paramètres cristallins obtenus sur diffractomètre Philips PW 1100 (anticathode au Cu) avec 25 réflexions 10 < θ < 17°. Mesure des intensités par 'flying stepscan', (logiciel Philips), angle de balayage de 1,65°, vitesse de scanning de 0,020° s^{-1} par pas de 3/100° en θ, domaine d'exploration de $2\theta \leq 136°$ ($-30 \leq h \leq 30$, $0 \leq k \leq 4$, $0 \leq l \leq 21$). Réflexions de référence $4\bar{1}2$, 404, $\bar{4}1\bar{2}$ mesurées toutes les heures avec des variations respectives d'intensité 1,1, 1,2, 1,1%. Corrections de Lorentz–polarisation. Les effets de l'absorption ont été négligés; résolution par méthodes directes: programme *SHELXS*86 (Sheldrick, 1986). Sur 3054 réflexions indépendantes, 3049 réflexions ont été retenues avec $\sin\theta/\lambda \geq 0{,}060$ Å^{-1}. Affinement des $F_{\rm obs}$ et des coefficients de température par moindres carrés et en matrice complète à l'aide d'une version modifiée de *ORFLS* (Busing, Martin & Levy, 1962). Les facteurs de diffusion atomique sont ceux des *International Tables for X-ray Crystallography* (1974, Tome IV) et pour l'hydrogène, ceux de Stewart, Davidson & Simpson (1965). Atomes H placés sur sections de Fourier-différence et affinés; en fin d'affinement avec des facteurs d'agitation thermique anisotrope pour tous les atomes sauf H, R = 0,067 (wR = 0,061 avec w = 1) pour 3049 réflexions retenues, S = 2,87 avec 91 paramètres, $(\Delta/\sigma)_{\rm max}$ pour les x, y, z des C, O: 0,083; $\Delta\rho$ = 0,13–0,16 e Å^{-3}. Programme utilisé pour les dessins: *ORTEP*II (Johnson, 1976). Ordinateur: Matra 570/CX.

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