identified by *rigid-molecule* energy-minimization calculations, itself suggests that distortion effects are likely to be small. In conclusion, therefore, we believe that the combined use of powder diffraction and energy minimization represents a powerful technique for structure solution in organic molecular systems. In future work we intend to extend their use to studies of related materials such as cyclohexanol and cyclohexanone.

We would like to express our thanks to Dr A. W. Hewat, Mr John Davies and Mr A. M. T. Bell for their expert assistance during the experiments. We have also benefitted from helpful discussions with G. S. Pawley. This work was funded in part by the SERC through access to research facilities at the Institut Laue–Langevin and Daresbury Laboratory.

References

ANDREW, E. R. & EADES, R. G. (1953). *Proc. R. Soc. London Ser. A*, **216**, 398–412.

BAHARIE, E. & PAWLEY, G. S. (1977). *J. Appl. Cryst.* **10**, 465–467.

BURNS, G. & DACOL, F. H. (1984). *Solid State Commun.* **51**, 773–775.

CRAIN, J., POON, W. C.-K., CAIRNS-SMITH, A. & HATTON, P. D. (1992). *J. Phys. Chem.* **96**, 8168–8173.

FITCH, A. N. & MURRAY, A. D. (1992). *PDPL*. An integrated powder diffraction program library. In preparation.

HAINES, J. & GILSON, D. F. R. (1989). *J. Phys. Chem.* 7920–7925.

HAINES, J. & GILSON, D. F. R. (1990). *J. Phys. Chem.* **94**, 4712–4716.

HEWAT, A. W. & BAILEY, I. (1976). *Nucl. Instrum. Methods*, **137**, 463.

KAHN, R., FOURME, R., ANDRÉ, D. & RENAUD, M. (1973). *Acta Cryst.* B**29**, 131–138.

MAYER, J., URBAN, S., HABRYLO, S., HOLDERNA, K., NATKANIEC, I., WÜRFLINGER, A. & ZAJAC, W. (1991). *Phys. Status Solidi*, B**166**, 381–394.

PAWLEY, G. S. (1980). *J. Appl. Cryst.* **13**, 630–633.

PAWLEY, G. S. (1981). *J. Appl. Cryst.* **14**, 357–361.

RENAUD, M. & FOURME, R. (1966). *J. Chim. Phys.* **62**, 27–32.

SCHULTE, L. & WÜRFLINGER, A. (1987). *J. Chem. Thermodyn.* **19**, 363–368.

WILDING, N. B., HATTON, P. D. & PAWLEY, G. S. (1991). *Acta Cryst.* B**47**, 797–806.

Acta Cryst. (1993). B**49**, 328–334

Structures of Four *N*-Benzoylaziridine and Aziridinium *p*-Toluenesulfonate Derivatives Grafted onto 7-Oxabicyclo[2.2.1]heptane Skeletons

BY A. ALAN PINKERTON,* ANTHONY C. GALLACHER, MARK RADIL AND ANDREAS KUNZE

Department of Chemistry of the University of Toledo, 2801 *W. Bancroft Street*, *Toledo*, *Ohio* 43606, *USA*

AND SUSY ALLEMANN AND PIERRE VOGEL*

Section de Chimie de l'Université de Lausanne, 2 *rue de la Barre*, *CH*-1005 *Lausanne*, *Switzerland*

(*Received* 2 *January* 1992; *accepted* 21 *July* 1992)

Abstract

Dimethyl 3-benzoyl-8-oxa-3-azatricyclo[3.2.1.$0^{2,4}$]octane-6,7-dicarboxylate (7), $C_{17}H_{17}NO_6$, $M_r = 331.33$, monoclinic, $P2_1/c$, $a = 5.362\,(1)$, $b = 24.558\,(3)$, $c = 11.793\,(1)$ Å, $\beta = 96.42\,(1)°$, $V = 1543\,(1)$ Å^3, $Z = 4$, $D_x = 1.43$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0.70930$ Å, $\mu = 1.0$ cm^{-1}, $F(000) = 696$, $T = 123\,(1)$ K, $R = 0.047$ for 1743 unique observed reflections. *cis*-6,7-Dimethoxycarbonyl-8-oxa-3-azoniatricyclo[3.2.1.$0^{2,4}$]octane *p*-toluenesulfonate (14), $C_{17}H_{21}NO_8S$, $M_r = 399.42$, monoclinic, $P2_1/c$, $a = 14.160\,(4)$, $b = 5.514\,(1)$, $c = 23.792\,(7)$ Å, $\beta = 100.16\,(2)°$, $V = 1828\,(2)$ Å^3, $Z = 4$, $D_x = 1.45$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0.70930$ Å, $\mu = 2.1$ cm^{-1}, $F(000) = 840$, $T = 193\,(1)$ K, $R = 0.045$ for 2737 unique observed reflections. *trans*-6,7-Dimethoxycarbonyl-8-oxa-3-azoniatricyclo[3.2.1.$0^{2,4}$]octane *p*-toluenesulfonate (18), $C_{17}H_{21}NO_8S$, $M_r = 399.42$, monoclinic, $P2_1/n$, $a = 21.501\,(6)$, $b = 5.476\,(2)$, $c = 15.858\,(2)$ Å, $\beta = 90.68\,(2)°$, $V = 1867\,(1)$ Å^3, $Z = 4$, $D_x = 1.42$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0.70930$ Å, $\mu = 2.1$ cm^{-1}, $F(000) = 840$, $T = 123\,(1)$ K, $R = 0.029$ for 1680 unique observed reflections. 3-Benzoyl-6-cyano-8-oxa-3-azatricyclo[3.2.1.$0^{2,4}$]oct-6-yl acetate (19), $C_{16}H_{14}N_2O_4$, $M_r = 298.30$, triclinic, $P\bar{1}$, $a = 5.654\,(1)$, $b = 8.088\,(3)$, $c = 16.223\,(7)$ Å, $\alpha = 103.78\,(3)$, $\beta = 90.35\,(3)$, $\gamma = 98.29\,(2)°$, $V = 712\,(1)$ Å^3, $Z = 2$, $D_x = 1.39$ g cm^{-3}, $\lambda(\text{Mo }K\alpha) = 0.70930$ Å, $\mu = 0.9$ cm^{-1}, $F(000) = 312$, $T = 294\,(1)$ K, $R = 0.040$ for 2021 unique observed reflections. The crystal structures of the aziridinium salts (14) and (18) and of the *N*-

---

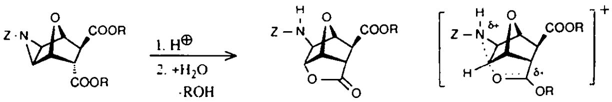
* To whom correspondence should be addressed

0108-7681/93/020328-07$06.00

benzoylaziridine derivatives (7) and (19) have been established by X-ray diffraction. The data are discussed in the light of proposed mechanisms for the acid-catalysed rearrangement of aziridine derivatives of 7-oxabicyclo[2.2.1]heptane diesters and compared with predictions from quantum mechanical calculations on aziridine and the aziridinium ion. The most striking observation is that the *endo* carboxylate group of salt (18) does not interact with the C centers of the aziridinium moiety. This result suggests that, contrary to common postulates, little positive charge resides on the C centers of aziridinium ions in their ground state.

Introduction

Alder & Stein (1933) reported that the treatment of the *N*-phenylaziridine derivative (1) (in which the two ester functions are in a *trans* relative configuration) with acetic anhydride gave the corresponding lactone (2) without skeleton rearrangement. Similar results were also obtained by Zefirov and co-workers (Zefirov, Kadzyauskas & Yur'ev, 1965; Zefirov, Kadzyauskas, Yur'ev & Bazarova, 1965) for the related carboxylic diacid (3) which gave the lactone acid (4) under the same conditions. Recently, we have applied this method of aminolactonization to aziridine derivatives (5) and (7) which led to the corresponding compounds (6) and (8), respectively (Allemann, Reymond & Vogel, 1990). These results were interpreted in terms of participation of the *endo* carboxylic function in the acid-promoted ring opening of the aziridine ring with the hypothetical transition state (9).

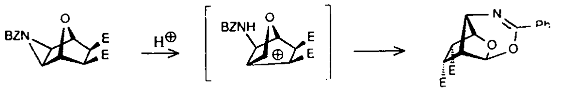


(1) $Z = Ph, R = Me$
(3) $Z = Ph, R = H$
(5) $Z = t\text{-BuOCO}, R = Me$
(7) $Z = PhCO, R = Me$
(17) $Z = H, R = Me$

(2) $Z = Ph, R = Me$
(4) $Z = Ph, R = H$
(6) $Z = t\text{-BuOCO}, R = Me$
(8) $Z = PhCO, R = Me$

(9)

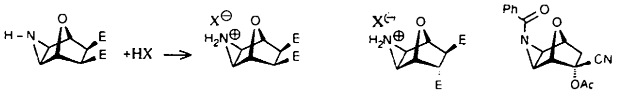
Under non-nucleophilic acidic media, the *N*-benzoylaziridine (10) was rearranged quantitatively into the 6,7-dihydro-1,3,5-dioxazepine (12). This process was interpreted in terms of a Wagner–Meerwein rearrangement involving the intermediacy of the oxycarbenium ion (11) (Allemann, Reymond & Vogel, 1990).



(10) (11) (12)

Owing to the inductive effects of the ethereal bridge and of the two *exo* ester moieties, the aziridinium ions (14)–(16) resulting from the protonation of the corresponding dimethyl 8-oxa-3-azatricyclo[3.2.1.0^{2,4}]octane-6,7-dicarboxylate (13) with non-nucleophilic acids were found to be stable at room temperature (Allemann, Reymond & Vogel, 1990). We have now found that protonation of the unprotected aziridine derivative (17), in which the two ester functions are in a *trans* configuration, can also give stable salts with non-nucleophilic acids (18). We thus have the possibility to examine by X-ray crystallography whether the aziridinium ions in these systems possess characteristics approaching those of the hypothetical transition states (9) and (11).

We may also study the changes induced in the molecular skeleton on protonation by comparing the cations with the structures of the uncharged species (7) (Allemann, Reymond & Vogel, 1990) and (19) (Allemann & Vogel, 1991), where the amine is protected as a benzamide.



(13)

(14) $X = p\text{-MeC}_6H_4SO_3$
(15) $X = (PhO)_2PO_2$
(16) $X = BF_4$

(18) $X = p\text{-MeC}_6H_4SO_3$

(19)

E=COOMe E=COOMe E=COOMe

Experimental

Compounds (7), (14) and (19) were prepared by literature methods (Allemann, Reymond & Vogel, 1990; Allemann & Vogel, 1991) and crystallized from ethanol/ether [(7), (14)] or CH_2Cl_2/ether/hexanes (19). (18) was prepared from (17) (Allemann, Reymond & Vogel, 1990) by addition of *p*-toluenesulfonic acid in ethanol. The precipitate was crystallized from ethanol/ether. Preliminary examination and X-ray intensity data collection for (7), (14), (18) and (19) were carried out with an Enraf–Nonius CAD-4 automatic diffractometer. The crystal data, intensity collection, structure solution and refinement methods are summarized in Table 1. For (7), two different crystals were used and the data scaled and averaged accordingly. The structures were solved by direct methods (*MULTAN*80; Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). All H atoms were located and, in the final least-squares refinement, non-H atoms were refined with anisotropic temperature factors and H atoms with isotropic temperature factors. All calculations were carried out on a VAX-11/750 computer, using *VAX/SDP* (Frenz, 1978). Scattering factors for the neutral atoms and anomalous-dispersion coefficients

Table 1. *Summary of crystal data, intensity measurement, structure solution and refinement*

	(7) [a]	(14)	(18)	(19)
Formula	$C_{17}H_{17}NO_6$	$C_{17}H_{21}NO_8S$ [b]	$C_{17}H_{21}NO_8S$ [b]	$C_{16}H_{14}N_2O_4$
M_r	331.33	399.42	399.42	298.30
Space group	$P2_1/c$	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	5.362 (1)	14.160 (4)	21.501 (6)	5.654 (1)
b (Å)	24.558 (3)	5.514 (1)	5.476 (2)	8.088 (3)
c (Å)	11.793 (1)	23.792 (7)	15.858 (2)	16.223 (7)
α (°)				103.78 (3)
β (°)	96.42 (1)	100.16 (2)	90.68 (2)	90.35 (3)
γ (°)				98.29 (2)
V (Å^3)	1543 (1)	1828 (2)	1867 (1)	712 (1)
Z	4	4	4	2
D_x (g cm^{-3})	1.43	1.45	1.42	1.39
Radiation (Å)	λ(Mo Kα) = 0.70930			
F(000)	696	840	840	312
T (K)	123 (1)	193 (1)	123 (1)	294 (1)
Maximum 2θ (°)	60.0	52.0	60.0	52.0
μ (cm^{-1})	1.0	2.1	2.1	0.9
Absorption correction	0.954 to 0.994	0.968 to 0.999	0.895 to 0.999	0.972 to 0.998
Decay correction	0.978 to 1.330	0.891 to 1.185	0.954 to 1.077	0.982 to 1.064
Reflections				
Total	8980	4130	4319	3070
Unique	4623	3968	2325	2771
$F_o^2 > 3.0\sigma(F_o^2)$	1743	2737	1680	2021
Experimental				
Color	Colorless			
Shape	Needle	Elongated plate	Plate	Irregular
Size (mm)	0.28 × 0.10 × 0.05	0.35 × 0.25 × 0.12	0.36 × 0.20 × 0.15	0.40 × 0.35 × 0.25
Diffractometer	Enraf–Nonius CAD-4			
Monochromator	Graphite crystal			
Scan technique	ω–2θ	ω–$(2/3)\theta$	ω–2θ	ω–2θ
Backgrounds	From analysis of the scan profile [c]			
Unit cell	From 25 reflections in the range $9 < \theta < 15$°			
Indices measured	$0 < h < 7$ $0 < k < 34$ $-16 < l < 16$	$0 < h < 17$ $0 < k < 6$ $-29 < l < 28$	$-29 < h < 29$ $0 < k < 7$ $-21 < l < 21$	$0 < h < 6$ $-9 < k < 9$ $-19 < l < 19$
$R_{\rm int}$ (%)	7.7	3.8	2.6	1.6
Solution	Direct methods [d]			
H atoms	Located and refined isotropically			
Refinement	Full-matrix least squares			
Function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$			
w	$4F_o^2/\sigma^2(F_o^2)$			
Parameters	285	328	328	252
R	0.047	0.045	0.029	0.040
wR	0.053	0.059	0.039	0.052
S	1.17	1.75	1.26	1.54
$(\Delta/\sigma)_{\rm max}$	0.06	0.10	0.86	0.03
$(\Delta\rho)_{\rm max}$ (e Å^{-3})	0.26 (7)	0.68 (7)	0.20 (4)	0.23 (4)
$(\Delta\rho)_{\rm min}$ (e Å^{-3})	−0.15 (7)	−0.15 (7)	−0.18 (4)	−0.22 (4)

Notes: (*a*) Two different crystals of similar size were used. (*b*) $[C_{10}H_{14}NO_5][C_7H_7O_3S]$. (*c*) Blessing, Coppens & Becker (1974). (*d*) *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980).

were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final atomic coordinates are given in Tables 2, 3, 4 and 5 for (7), (14), (18) and (19), respectively. Selected bond lengths, and angles are given in Table 6. Perspective drawings (*ORTEP*II; Johnson, 1976) of molecules (7), (14), (18) and (19) are shown in Figs. 1, 2, 3 and 4.*

Discussion

The atom numbering for the molecules given in Figs. 1–4 does not follow IUPAC rules. This allows us to use a consistent numbering scheme for all four tricyclic skeletons.

The oxycarbenium ion (11) was postulated to be the intermediate in the rearrangement of (10) to (12). If the hyperconjugative interaction (14)$\longleftrightarrow$(14′)$\longleftrightarrow$(14″) were an important contribution to the positive charge delocalization as in (11), elongation of the bonds C1—C6 [1.560 (3) Å] and C4—C5 [1.537 (3) Å] should be found in (14). In fact, these distances are not significantly different from the same bonds in the benzamides (7) and (19)

---

* Lists of calculated and observed structure factors, synthetic and spectroscopic details, anisotropic thermal parameters, and complete tables of distances, angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55727 (118 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0420]

Table 2. *Positional parameters for* (7)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(8\pi^2/3)$ trace **U**.

	x	y	z	B (Å^2)
O1	0.7298 (3)	0.01098 (9)	0.6722 (2)	1.65 (4)
O2	1.0344 (3)	0.12520 (9)	0.2367 (2)	1.98 (4)
O3	0.7840 (3)	0.05352 (9)	0.1915 (2)	1.82 (4)
O4	0.3317 (3)	0.22226 (9)	0.4140 (2)	1.67 (4)
O5	0.4753 (3)	0.21498 (9)	0.2425 (2)	1.78 (4)
O7	0.5531 (3)	0.10387 (9)	0.5166 (2)	1.29 (3)
N8	0.9874 (4)	0.0772 (1)	0.6167 (2)	1.29 (4)
C1	0.7109 (4)	0.1511 (1)	0.5190 (2)	1.20 (5)
C2	0.9719 (4)	0.1273 (1)	0.5498 (2)	1.31 (5)
C3	0.9540 (4)	0.0725 (1)	0.4930 (2)	1.29 (4)
C4	0.6826 (4)	0.0720 (1)	0.4387 (2)	1.21 (4)
C5	0.6629 (4)	0.1102 (1)	0.3332 (2)	1.19 (4)
C6	0.6980 (4)	0.1670 (1)	0.3921 (2)	1.18 (4)
C9	0.8522 (4)	0.0990 (1)	0.2501 (2)	1.24 (4)
C10	0.9484 (5)	0.0375 (2)	0.1081 (3)	2.26 (6)
C11	0.4807 (4)	0.2044 (1)	0.3539 (2)	1.31 (5)
C12	0.2716 (6)	0.2493 (2)	0.1942 (3)	2.54 (6)
C13	0.8096 (4)	0.0578 (1)	0.6843 (2)	1.28 (5)
C14	0.7503 (4)	0.0928 (1)	0.7804 (2)	1.31 (5)
C15	0.8938 (5)	0.1387 (1)	0.8155 (3)	1.70 (5)
C16	0.8334 (6)	0.1697 (1)	0.9065 (3)	2.26 (6)
C17	0.6308 (5)	0.1556 (2)	0.9645 (3)	2.31 (6)
C18	0.4894 (5)	0.1104 (2)	0.9298 (3)	2.51 (6)
C19	0.5461 (4)	0.0788 (1)	0.8385 (2)	1.93 (6)
H1	0.646 (5)	0.179 (1)	0.568 (3)	1.2 (6)*
H2	1.120 (5)	0.146 (1)	0.553 (3)	1.3 (6)*
H3	1.084 (5)	0.061 (1)	0.457 (2)	1.2 (6)*
H4	0.609 (5)	0.037 (1)	0.425 (2)	0.9 (6)*
H5	0.487 (5)	0.107 (1)	0.291 (2)	0.7 (5)*
H6	0.847 (5)	0.185 (1)	0.374 (3)	1.8 (7)*
H7	1.115 (6)	0.036 (2)	0.149 (3)	3.2 (9)*
H8	0.882 (6)	0.007 (2)	0.077 (3)	4 (1)*
H9	0.944 (6)	0.068 (1)	0.045 (3)	2.5 (8)*
H10	0.105 (7)	0.228 (2)	0.209 (3)	3.6 (9)*
H11	0.291 (6)	0.252 (1)	0.110 (4)	4 (1)*
H12	0.283 (6)	0.286 (2)	0.227 (3)	3.8 (9)*
H13	1.037 (5)	0.149 (1)	0.772 (3)	1.9 (7)*
H14	0.919 (7)	0.201 (2)	0.926 (3)	3.7 (9)*
H15	0.585 (6)	0.179 (1)	1.026 (3)	2.7 (8)*
H16	0.358 (5)	0.100 (1)	0.968 (2)	1.6 (6)*
H17	0.451 (5)	0.048 (1)	0.819 (3)	1.8 (7)*

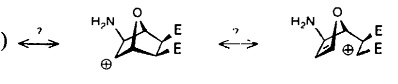
Table 3. *Positional parameters for* (14)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(8\pi^2/3)$ trace **U**.

	x	y	z	B (Å^2)
S1	0.29886 (4)	0.1203 (1)	0.43665 (2)	1.93 (1)
O1	0.3583 (1)	0.3231 (3)	0.46103 (7)	2.31 (3)
O2	0.3376 (1)	−0.0006 (4)	0.39118 (8)	3.14 (4)
O3	0.2770 (1)	−0.0431 (4)	0.47977 (8)	3.43 (4)
O7	0.4477 (1)	0.7566 (3)	0.60174 (6)	1.81 (3)
O10	0.4110 (1)	1.0179 (3)	0.72479 (7)	2.35 (3)
O11	0.2833 (1)	0.7985 (4)	0.73917 (7)	2.63 (4)
O14	0.2418 (1)	0.9894 (3)	0.62272 (8)	2.83 (4)
O15	0.1622 (1)	0.6999 (3)	0.56738 (7)	2.43 (3)
N8	0.5338 (2)	0.3651 (4)	0.58806 (8)	2.09 (4)
C1	0.3769 (2)	0.5806 (4)	0.57844 (9)	1.78 (4)
C2	0.4303 (2)	0.3423 (4)	0.58879 (9)	1.82 (4)
C3	0.4985 (2)	0.3897 (5)	0.64247 (9)	1.90 (4)
C4	0.4755 (2)	0.6481 (5)	0.65728 (9)	1.82 (4)
C5	0.3802 (2)	0.6260 (4)	0.67941 (9)	1.65 (4)
C6	0.3076 (2)	0.5847 (4)	0.62268 (9)	1.63 (4)
C9	0.3612 (2)	0.8416 (5)	0.71523 (9)	1.84 (4)
C12	0.2552 (2)	0.9913 (6)	0.7737 (1)	3.41 (6)
C13	0.2351 (2)	0.7835 (5)	0.60566 (9)	1.87 (4)
C16	0.0912 (2)	0.8783 (6)	0.5436 (1)	3.28 (6)
C17	0.1885 (2)	0.2486 (4)	0.40257 (9)	1.86 (4)
C18	0.1339 (2)	0.1353 (5)	0.3560 (1)	2.46 (5)
C19	0.0472 (2)	0.2359 (6)	0.3306 (1)	2.77 (5)
C20	0.0141 (2)	0.4511 (5)	0.3505 (1)	2.56 (5)
C21	0.0698 (2)	0.5619 (5)	0.3970 (1)	2.91 (6)
C22	0.1570 (2)	0.4633 (5)	0.4228 (1)	2.68 (5)
C23	−0.0791 (2)	0.5651 (7)	0.3218 (1)	3.68 (7)
H1	0.355 (2)	0.618 (5)	0.538 (1)	2.3 (6)*
H2	0.407 (2)	0.190 (5)	0.576 (1)	2.1 (5)*
H3	0.520 (2)	0.260 (6)	0.669 (1)	3.8 (7)*
H4	0.525 (2)	0.740 (5)	0.680 (1)	2.6 (6)*
H5	0.383 (1)	0.484 (4)	0.7006 (9)	1.0 (4)*
H6	0.278 (2)	0.435 (5)	0.622 (1)	2.1 (5)*
H18	0.152 (2)	−0.014 (5)	0.346 (1)	2.0 (5)*
H19	0.016 (2)	0.156 (6)	0.296 (1)	4.6 (8)*
H21	0.042 (2)	0.705 (6)	0.412 (1)	3.8 (7)*
H22	0.198 (2)	0.544 (6)	0.447 (1)	3.4 (6)*
H81	0.565 (2)	0.216 (6)	0.590 (1)	4.0 (7)*
H82	0.553 (2)	0.489 (5)	0.577 (1)	2.9 (6)*
H121	0.197 (2)	0.948 (6)	0.780 (1)	4.3 (8)*
H122	0.305 (2)	1.010 (6)	0.805 (1)	4.3 (7)*
H123	0.255 (2)	1.150 (7)	0.757 (1)	5.9 (9)*
H161	0.064 (3)	0.809 (9)	0.511 (2)	9 (1)*
H162	0.053 (3)	0.942 (8)	0.578 (2)	7 (1)*
H163	0.124 (2)	0.988 (6)	0.520 (1)	4.1 (7)*
H231	−0.108 (2)	0.658 (6)	0.351 (1)	4.9 (8)*
H232	−0.074 (2)	0.682 (7)	0.298 (2)	6.0 (9)*
H233	−0.129 (3)	0.435 (8)	0.307 (2)	7 (1)*

[1.541 (4) and 1.552 (4) Å for (7) and 1.559 (2) and 1.532 (3) Å for (19), respectively]. Thus the charge delocalization (14)⟷(14′)⟷(14″) appears to be negligible. The same statement can also be made for the aziridinium salt (18) as the bond lengths are also similar [C1—C6 1.539 (3); C4—C5 1.536 (3) Å].

(14)



(14′) (14″)

The facile lactonizations (1)→(2), (3)→(4), (5)→(6) and (7)→(8) [transition state of type (9)] suggested that either the C═O or the OMe moiety of the *endo* ester group should interact with the carbon center C2 of the aziridinium ion (18). To our surprise, the crystal structure of (18) shows a conformation for this *endo*-COOMe function avoiding any intramolecular interaction with the bridged cationic system and thus does not resemble in any way that suggested by transition state (9). This result can be interpreted in terms of little positive charge residing on the aziridine C centers in the ground state of (18). One might anticipate that, in the unsymmetrical molecules, the C—N bonds of the three-membered ring would be differentiated. Although there is some evidence for this, the differences are not significant (Table 6).

Quantum mechanical calculations (Hartree–Fock level, Pople's 6-31 G^* basis set, completely optimized geometries) showed that on going from aziridine (20) to aziridinium ion (21), the C—C bond is slightly shortened and the C—N bonds slightly lengthened (Cremer & Kraka, 1985). The calculations also predicted a larger bond order for the C—C bond in (21)

Table 4. *Positional parameters for* (18)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(8\pi^2/3)$ trace **U**.

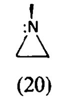
	x	y	z	B (Å^2)
S	0.46173 (3)	0.0636 (1)	0.64430 (4)	1.55 (1)
O1	0.41321 (8)	−0.1087 (4)	0.6241 (1)	2.23 (4)
O2	0.46495 (7)	0.2658 (3)	0.5847 (1)	1.83 (4)
O3	0.52312 (8)	−0.0459 (4)	0.6585 (1)	2.02 (4)
O4	0.20608 (8)	0.2929 (4)	0.2789 (1)	2.97 (4)
O5	0.15380 (8)	0.4883 (4)	0.3796 (1)	2.62 (4)
O6	0.24744 (9)	0.8438 (4)	0.5271 (1)	2.50 (4)
O7	0.33463 (7)	0.2004 (3)	0.3994 (1)	1.57 (3)
O8	0.27356 (9)	0.5546 (4)	0.6206 (1)	2.63 (4)
N8	0.43000 (9)	0.4648 (4)	0.4150 (1)	1.53 (4)
C1	0.3330 (1)	0.3119 (5)	0.4811 (2)	1.59 (5)
C2	0.3796 (1)	0.5197 (5)	0.4739 (2)	1.43 (5)
C3	0.3730 (1)	0.5902 (5)	0.3837 (2)	1.44 (5)
C4	0.3237 (1)	0.4176 (5)	0.3508 (2)	1.49 (5)
C5	0.2624 (1)	0.5152 (5)	0.3863 (2)	1.47 (5)
C6	0.2683 (1)	0.4322 (5)	0.4804 (2)	1.42 (5)
C9	0.2616 (1)	0.6357 (5)	0.5427 (2)	1.78 (6)
C10	0.2715 (2)	0.7415 (7)	0.6860 (2)	3.97 (8)
C11	0.2061 (1)	0.4165 (5)	0.3413 (2)	1.85 (5)
C12	0.0961 (1)	0.4083 (7)	0.3399 (2)	3.24 (7)
C13	0.4427 (1)	0.1927 (5)	0.7438 (2)	1.52 (5)
C14	0.4062 (1)	0.0664 (5)	0.7990 (2)	1.92 (6)
C15	0.3953 (1)	0.1573 (6)	0.8788 (2)	2.41 (6)
C16	0.4199 (1)	0.3793 (6)	0.9044 (2)	2.18 (6)
C17	0.4565 (1)	0.5053 (5)	0.8472 (2)	2.22 (6)
C18	0.4673 (1)	0.4165 (5)	0.7674 (2)	1.97 (6)
C19	0.4081 (1)	0.4801 (7)	0.9905 (2)	3.35 (7)
H1	0.341 (1)	0.204 (5)	0.521 (1)	1.8 (5)*
H2	0.236 (1)	0.306 (4)	0.493 (1)	1.1 (5)*
H3	0.257 (1)	0.688 (5)	0.383 (1)	1.9 (5)*
H4	0.326 (1)	0.384 (4)	0.292 (1)	0.8 (5)*
H5	0.381 (1)	0.745 (4)	0.367 (1)	0.9 (5)*
H6	0.3906 (9)	0.637 (4)	0.520 (1)	0.8 (5)*
H7	0.435 (1)	0.308 (5)	0.396 (1)	2.3 (6)*
H8	0.466 (1)	0.569 (5)	0.417 (2)	3.6 (7)*
H9	0.232 (1)	0.770 (6)	0.697 (2)	4.3 (7)*
H10	0.281 (2)	0.660 (8)	0.738 (2)	7 (1)*
H11	0.291 (1)	0.905 (6)	0.668 (2)	3.7 (7)*
H12	0.093 (1)	0.486 (5)	0.288 (2)	2.8 (6)*
H13	0.058 (1)	0.479 (6)	0.375 (2)	5.5 (9)*
H14	0.101 (2)	0.232 (7)	0.336 (2)	6.4 (9)*
H15	0.390 (1)	−0.080 (5)	0.785 (1)	1.7 (5)*
H16	0.370 (1)	0.064 (6)	0.918 (2)	3.6 (7)*
H17	0.473 (1)	0.655 (5)	0.864 (1)	1.7 (5)*
H18	0.486 (1)	0.503 (5)	0.728 (2)	3.9 (7)*
H19	0.392 (2)	0.616 (9)	0.990 (2)	9 (1)*
H20	0.386 (1)	0.385 (6)	1.024 (2)	5.0 (8)*
H21	0.442 (2)	0.545 (9)	1.022 (3)	11 (1)*

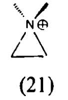
Table 5. *Positional parameters for* (19)

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(8\pi^2/3)$ trace **U**.

	x	y	z	B (Å^2)
O7	0.4472 (2)	0.1669 (1)	0.70099 (7)	2.92 (2)
O9	−0.0485 (2)	−0.1719 (1)	0.63824 (8)	3.29 (2)
O11	0.1619 (2)	−0.3552 (2)	0.6784 (1)	4.94 (3)
O14	0.6018 (2)	0.1907 (2)	0.88334 (8)	4.04 (3)
N8	0.2338 (3)	0.2294 (2)	0.84284 (9)	3.32 (3)
N23	0.4188 (3)	−0.2176 (3)	0.5099 (1)	5.42 (4)
C1	0.3271 (3)	0.0090 (2)	0.7153 (1)	2.76 (3)
C2	0.1550 (3)	0.0661 (2)	0.7840 (1)	3.10 (3)
C3	0.1002 (3)	0.2306 (2)	0.7666 (1)	3.32 (4)
C4	0.2388 (3)	0.2422 (2)	0.6883 (1)	3.14 (3)
C5	0.1053 (3)	0.1079 (2)	0.6135 (1)	3.40 (4)
C6	0.1701 (3)	−0.0605 (2)	0.6315 (1)	3.00 (3)
C10	−0.0281 (3)	−0.3205 (2)	0.6613 (1)	3.38 (4)
C12	−0.2635 (4)	−0.4246 (3)	0.6641 (2)	4.97 (5)
C13	0.4728 (3)	0.2888 (2)	0.8682 (1)	3.00 (3)
C16	0.5523 (3)	0.4782 (2)	0.8851 (1)	2.83 (3)
C17	0.4110 (3)	0.5935 (2)	0.8682 (1)	3.69 (4)
C18	0.4955 (4)	0.7678 (2)	0.8877 (1)	4.25 (4)
C19	0.7197 (4)	0.8288 (2)	0.9248 (1)	4.24 (4)
C20	0.8624 (4)	0.7155 (3)	0.9422 (1)	4.32 (4)
C21	0.7799 (3)	0.5410 (2)	0.9221 (1)	3.58 (4)
C22	0.3098 (3)	−0.1520 (2)	0.5630 (1)	3.68 (4)
H1	0.444 (2)	−0.062 (2)	0.7263 (9)	1.9 (3)*
H2	0.042 (3)	−0.014 (2)	0.803 (1)	3.3 (4)*
H3	−0.051 (3)	0.262 (2)	0.773 (1)	3.5 (4)*
H4	0.284 (3)	0.352 (2)	0.678 (1)	3.7 (4)*
H17	0.257 (3)	0.556 (2)	0.843 (1)	4.0 (4)*
H18	0.399 (3)	0.849 (3)	0.877 (1)	5.7 (5)*
H19	0.773 (3)	0.957 (2)	0.940 (1)	4.8 (4)*
H20	1.015 (3)	0.754 (3)	0.969 (1)	5.4 (5)*
H21	0.882 (3)	0.462 (2)	0.934 (1)	4.1 (4)*
H51	0.162 (3)	0.125 (2)	0.560 (1)	4.2 (4)*
H52	−0.068 (3)	0.104 (2)	0.613 (1)	3.8 (4)*
H121	−0.251 (4)	−0.539 (3)	0.659 (2)	6.6*
H122	−0.369 (4)	−0.359 (3)	0.687 (1)	6.6*
H123	−0.351 (4)	−0.441 (3)	0.612 (2)	6.6*

(1.18) than in (20) (1.06) and a smaller bond order for C—N bonds in (21) (0.77) than in (20) (0.97). Our data for (7), (14), (18) and (19) (Table 6) show the same trend as these calculations. The longer C—C bonds in the current study are most likely due to the additional strain introduced by grafting the three-membered ring onto a bicyclo[2.2.1]heptane skeleton.


(20)


(21)

Possible hydrogen bonding between the ethereal bridge of the 7-oxabicyclo[2.2.1]heptane skeleton and the *syn*-NH bond of the adjacent aziridinium ion in (14) and (18) is weak [O···H: 2.25 (14), 2.24 Å (18)], if it exists at all. Both the *syn*- and *anti*-H(N) atoms are preferentially hydrogen bonded to two different tosylate (*p*-methylbenzenesulfonate) counter ions in these salts, each tosylate being bonded to two different aziridinium ions.

It is interesting to note that the benzoyl group in benzamides (7) and (19) is *syn* with respect to the ethereal O bridge of the 7-oxabicyclo[2.2.1]heptane system and oriented in such a way as to maximize the electrostatic interaction between the carbonyl group and the ethereal moiety. This interpretation is in accord with the fact that the carbonyl bond of the benzamide deviates from the CCN plane by 6.9° (7) and 5.9° (19).

The tosylate counter ions have no unusual features.

Concluding remarks

X-ray crystal structures of aziridium salts (14) and (18) and of the *N*-benzoylaziridine derivatives (7) and (19) are in accord with predictions based on

Table 6. *Selected bond distances* (Å) *and angles* (°)

			(7)	(14)	(18)	(19)
O7	C1		1.434 (3)	1.435 (3)	1.433 (3)	1.428 (2)
O7	C4		1.443 (3)	1.441 (3)	1.436 (3)	1.437 (2)
N8	C2		1.459 (4)	1.475 (3)	1.471 (3)	1.441 (2)
N8	C3		1.455 (3)	1.474 (3)	1.485 (3)	1.448 (2)
C1	C2		1.523 (3)	1.514 (3)	1.521 (4)	1.517 (3)
C1	C6		1.541 (4)	1.560 (3)	1.539 (3)	1.559 (2)
C2	C3		1.501 (5)	1.482 (3)	1.487 (3)	1.498 (3)
C3	C4		1.523 (3)	1.517 (4)	1.509 (4)	1.512 (3)
C4	C5		1.552 (4)	1.537 (3)	1.536 (3)	1.532 (3)
C5	C6		1.562 (4)	1.562 (3)	1.563 (4)	1.551 (3)
C1	O7	C4	97.3 (2)	97.6 (2)	97.3 (2)	97.8 (1)
C2	N8	C3	62.0 (2)	60.3 (1)	60.4 (2)	62.5 (1)
O7	C1	C2	102.6 (2)	103.2 (2)	103.2 (2)	103.8 (1)
O7	C1	C6	102.9 (2)	102.1 (2)	102.0 (2)	100.4 (1)
C2	C1	C6	105.6 (2)	104.9 (2)	106.0 (2)	105.6 (1)
N8	C2	C1	116.6 (2)	113.1 (2)	112.7 (2)	115.5 (1)
N8	C2	C3	58.8 (2)	59.8 (1)	60.3 (2)	59.0 (1)
C1	C2	C3	103.1 (2)	102.6 (2)	102.2 (2)	102.3 (1)
N8	C3	C2	59.1 (2)	59.9 (1)	59.3 (2)	58.5 (1)
N8	C3	C4	115.3 (2)	114.2 (2)	113.6 (2)	117.8 (2)
C2	C3	C4	101.8 (2)	103.4 (2)	103.2 (2)	102.8 (1)
O7	C4	C3	103.5 (2)	102.2 (2)	102.9 (2)	102.7 (1)
O7	C4	C5	100.9 (2)	103.5 (2)	103.1 (2)	102.4 (1)
C3	C4	C5	108.0 (2)	104.0 (2)	104.9 (2)	107.0 (2)
C4	C5	C6	100.9 (2)	101.5 (2)	100.9 (2)	100.8 (1)
C1	C6	C5	101.2 (2)	100.9 (2)	101.2 (2)	101.9 (1)

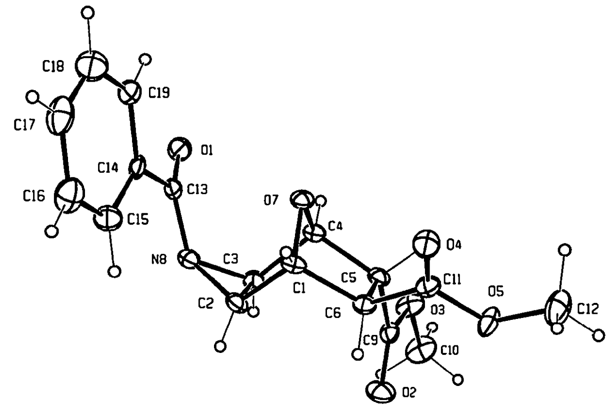


Fig. 1. Perspective drawing of aziridine (7) (50% probability ellipsoids for non-H atoms).

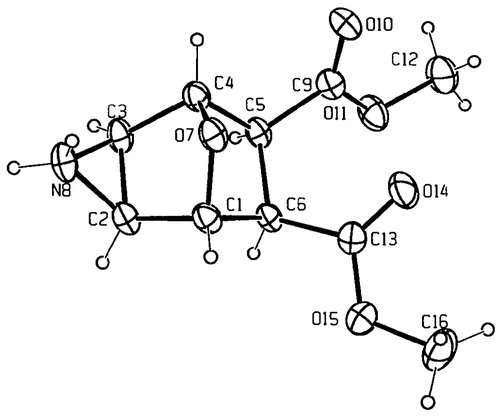


Fig. 2. Perspective drawing of aziridinium ion (14) (50% probability ellipsoids for non-H atoms).

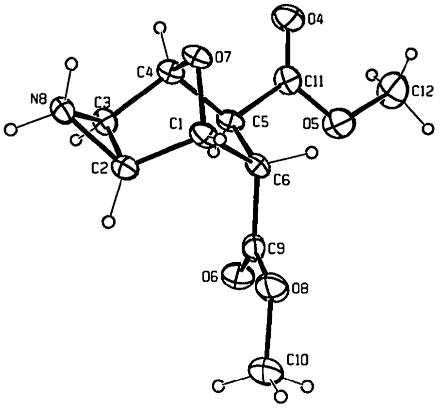


Fig. 3. Perspective drawing of aziridinium ion (18) (50% probability ellipsoids for non-H atoms).

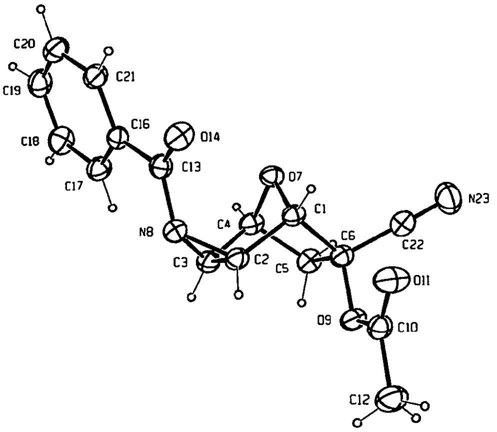


Fig. 4. Perspective drawing of aziridine (19) (30% probability ellipsoids for non-H atoms).

quantum mechanical calculations that protonation of an aziridine induces a small shortening of the C—C bond and a small lengthening of the C—N bonds. In the solid state, the *endo*-COOMe group of (18) has an orientation which is consistent with only a small positive charge density residing on the carbon centers of the aziridinium moiety. This hypothesis is confirmed by the observation that the C—C bonds in (14) and (18) which hyperconjugate with the C—N bonds are not elongated in a significant fashion.

We thank the College of Arts and Sciences of the University of Toledo for generous support of the X-ray facility.

References

Alder, K. & Stein, G. (1933). *Justus Liebigs Ann. Chem.* **504**, 216–257.

Allemann, S., Reymond, J.-L. & Vogel, P. (1990). *Helv. Chim. Acta*, **73**, 674–689.

Allemann, S. & Vogel, P. (1991). *Synthesis*, **11**, 923–928.

Blessing, R. H., Coppens, P. & Becker, P. (1974). *J. Appl. Cryst.* **7**, 488–492.

Cremer, D. & Kraka, E. (1985). *J. Am. Chem. Soc.* **107**, 3800–3810.

Frenz, B. A. (1978). *The Enraf–Nonius CAD-4 SDP – a Real-Time System for Concurrent X-ray Data Collection and Crystal Structure Determination.* In *Computing in Crystallography*, edited by H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld & G. C. Bassi, pp. 64–71. Delft Univ. Press.

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

Zefirov, N. S., Kadzyauskas, P. P. & Yur'ev, Yu. K. (1965). *Zh. Obshch. Khim.* **35**, 259–264.

Zefirov, N. S., Kadzyauskas, P. P., Yur'ev, Yu. K. & Bazarova, V. N. (1965). *Zh. Obshch. Khim.* **35**, 1499–1500.

Acta Cryst. (1993). **B49**, 334–342

Synthesis and Crystal Structure of Guanidinium L-Monohydrogentartrate: Encapsulation of an Optically Nonlinear Octupolar Cation

By J. Zyss

Departement d'Electronique Quantique et Moléculaire, CNET, 196 *Avenue Henri-Ravera,* 92220 *Bagneux, France*

and J. Pecaut, J. P. Levy and R. Masse

Laboratoire de Cristallographie associé à l'Université Joseph Fourier, CNRS, BP 166,
38042 *Grenoble CEDEX* 09, *France*

(*Received* 27 *January* 1992; *accepted* 3 *August* 1992)

Abstract

Encapsulation of an optically nonlinear octupolar guanidinium cation in a host polyanionic L-monohydrogentartrate lattice leads to a noncentrosymmetric orthorhombic $P2_12_12_1$ guest–host crystalline structure with cell parameters $a = 11.347$ (2), $b = 11.162$ (2), $c = 6.668$ (2) Å with $Z = 4$. Final $R = 0.049$ from 1229 independent reflections. The packing shows strong interlocking between the anionic and cationic sublattices by a multidirectional hydrogen-bonding network. The optimally oriented octupolar crystalline structure for the 222 crystal point group is defined and the corresponding reference maximal nonlinear susceptibility is compared to that of the present guanidinium crystal structure thus pointing out possible improvements *via* appropriate structural modifications.

Introduction

The engineering of guanidinium L-monohydrogentartrate $[C(NH_2)_3^+.C_4H_5O_6^-]$ single crystals follows a new direction in the conception of quadratic nonlinear optical materials. Over the last ten years organic materials made up of molecules containing polarizable π-electron systems asymetrized by interacting electron donor and acceptor groups have been extensively developed. Nitroaniline derivatives (Nicoud & Twieg, 1987; Oudar & Hierle, 1977; Zyss, Chemla & Nicoud, 1981; Zyss, Nicoud & Coquillay, 1984), stilbenes (Wang, Tam, Stevenson, Clement & Calabrese, 1988; Tam, Guerin, Calabrese & Stevenson, 1989), cyanobiphenyls (Zyss, Ledoux, Bertault & Toupet, 1991), push–pull polyenes (Barzoukas, Blanchard-Desce, Josse, Lehn & Zyss, 1989) and polyphenyls (Ledoux, Zyss, Jutand & Amatore, 1991) are noteworthy molecules for quadratic nonlinear optical applications. The variety of chemical substitutions provided by organic chemistry guided by empirical as well as more elaborate theoretical models has allowed for the targeted tailoring of optimized crystals towards quadratic nonlinear optics (Zyss & Oudar, 1982; Zyss & Chemla, 1987). Molecular nonlinear evaluations from the EFISH experiment (Levine & Bethea, 1974; Oudar & Le Person, 1975, 1976; Ledoux & Zyss, 1982), related by an oriented gas model, have been very useful for selective development of such crystals. Besides purely crystallographic structural considerations, the spectral adequacy of crystals has also been discussed, in view of applications, in terms of a 'transparency-efficiency' trade-off based on both molecular (Zyss, 1991*a*) and excitonic considerations (Zyss, Ledoux,

0108-7681/93/020334-09$06.00