Table 3. *Interatomic distances* (Å) *and bond angles* (°) *of* BF_4^- *anions and* C_2H_5OH

B(73)–F(74)	1·30 (1)	B(78)–F(80)	1·33 (3)
B(73)–F(75)	1·32 (2)	B(78)–F(81)	1·28 (2)
B(73)–F(76)	1·28 (2)	B(78)–F(82)	1·19 (2)
B(73)–F(77)	1·25 (2)	C(83)–C(84)	1·44 (2)
B(78)–F(79)	1·23 (2)	C(83)–O(85)	1·21 (3)
F(74)–B(73)–F(75)	109 (1)	F(79)–B(78)–F(81)	116 (1)
F(74)–B(73)–F(76)	111 (1)	F(79)–B(78)–F(82)	105 (1)
F(74)–B(73)–F(77)	110 (1)	F(80)–B(78)–F(81)	97 (1)
F(75)–B(73)–F(76)	110 (1)	F(80)–B(78)–F(82)	113 (2)
F(75)–B(73)–F(77)	107 (1)	F(81)–B(78)–F(82)	117 (1)
F(76)–B(73)–F(77)	111 (1)	C(84)–C(83)–O(85)	125 (1)
F(79)–B(78)–F(80)	108 (1)		

is shorter than those of DBTTF cations, which are 1·404 (7) Å (Honda, Katayama, Tanaka & Tanaka, 1985*a*) and 1·397 (6) Å (Honda, Katayama, Tanaka & Tanaka, 1985*b*). For molecule (IV), the central C=C bond length is comparable with that of the neutral molecule. Table 3 shows the bond lengths and bond angles of the BF_4^- anions and ethanol.

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The Structures of Tetracyclo[4.4.0.0^{2,8}.0^{4,7}]dec-9-en-5-one 2,4-Dinitrophenylhydrazone, (2), 10-Bromotricyclo[5.2.1.0^{4,8}]dec-5-en-2-one, (3), and Tetracyclo[5.3.0.0^{2,5}.0^{4,8}]dec-9-en-3-yl 3,5-Dinitrobenzoate, (4)

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Abstract. $C_{16}H_{14}N_4O_4$, (2), $M_r = 326{\cdot}3$, monoclinic, $P2_1/n$, $a = 6{\cdot}745$ (5), $b = 24{\cdot}915$ (8), $c = 8{\cdot}911$ (8) Å, $\beta = 99{\cdot}0$ (1)°, $V = 1480$ (2) Å^3, $Z = 4$, $D_x = 1{\cdot}47$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}01$ cm^{-1}, $F(000) = 680$, $T = 290$ K, $R(F) = 0{\cdot}080$ for 524 unique reflections [$I > 2{\cdot}5\sigma(I)$] and 118 variables. $C_{10}H_{11}BrO$, (3), $M_r = 227{\cdot}1$, monoclinic, $P2_1/c$, $a = 11{\cdot}088$ (3), $b = 6{\cdot}649$ (2), $c = 12{\cdot}667$ (3) Å, $\beta = 102{\cdot}36$ (3)°, $V = 912{\cdot}2$ (7) Å^3, $Z = 4$, $D_x = 1{\cdot}65$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 44{\cdot}08$ cm^{-1}, $F(000) = 456$, $T = 290$ K, $R(F) = 0{\cdot}048$ for 987 unique reflections [$I > 3\sigma(I)$] and 153 variables. $C_{17}H_{14}N_2O_6$, (4), $M_r = 342{\cdot}3$, triclinic, $P\bar{1}$, $a = 6{\cdot}428$ (2), $b = 9{\cdot}912$ (3), $c = 12{\cdot}455$ (3) Å, $\alpha = 94{\cdot}74$ (3), $\beta = 92{\cdot}64$ (3), $\gamma = 102{\cdot}79$ (3)°, $V = 769{\cdot}5$ (7) Å^3, $Z = 2$, $D_x = 1{\cdot}48$ g cm^{-3}, Mo $K\alpha$ radiation, $\lambda = 0{\cdot}71069$ Å, $\mu = 1{\cdot}23$ cm^{-1}, $F(000) = 356$, $T = 290$ K, $R(F) = 0{\cdot}032$ for 1562 unique reflections [$I > 3\sigma(I)$] and 268 variables. An investigation was undertaken of possible orbital interaction between

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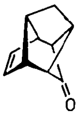
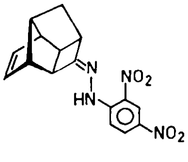
0108-2701/85/111638-05$01.50

orthogonal C=C and C=O bonds. Two of the three structures presented appear to have rearranged cage structures compared to the parent compound. The third one, having the parent compound cage structure, presents evidence for the supposed interaction in the form of a short distance of 2·90 Å between the carbonyl carbon and the olefinic bond. This structure served as a starting model for a molecular-mechanics calculation on the parent compound.

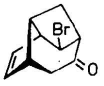
Introduction. Recently, the molecule tetracyclo-[5.3.0.0^{2,5}.0^{4,8}]dec-9-en-3-one, (1), a system containing two orthogonally oriented double bonds at a relatively short distance, has been prepared in our laboratory (Klunder, Schellekens & Zwanenburg, 1982). The UV spectrum of this compound [$\lambda(m)$ 204 nm ε 3200 l mol^{-1} cm^{-1} (n-hexane)] suggests a considerable orbital interaction. To establish the geometry of this molecule and the distance between the C=C bond and the C=O group, X-ray crystallographic characterization of the compound is needed. Unfortunately, we have not been able to grow X-ray-quality crystals of (1), which prompted us to synthesize crystalline derivatives to study this interesting interaction. The first attempt was the preparation of a hydrazone of (1) by treating (1) with 2,4-dinitrophenylhydrazine in methanol in the presence of sulfuric acid. The resulting orange crystalline compound (2) appeared to be a rearranged product, prompting further investigation of the acid-catalyzed rearrangement reactions of (1). This investigation resulted in the preparation of (3) by treatment of (1) with HBr in methanol. The preparation of derivatives of (1) in an acidic environment being unsuccessful, we attempted the preparation of a dinitro ester by reduction of (1) with $LiAlH_4$ and subsequent reaction with 3,5-dinitrobenzoyl chloride in the presence of pyridine, which resulted in the crystalline dinitro ester (4). We herein report the X-ray crystallographic characterization of (2), (3) and (4). A full account of the synthetic work and mechanistic considerations is available elsewhere (Klunder, Schellekens & Zwanenburg, 1982; Sakkers, Vankan, Klunder & Zwanenburg, 1979), or will be published soon.



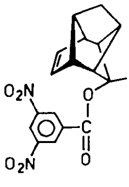
(1)



(2)



(3)



(4)

Experimental. All three structures: Enraf–Nonius CAD-4 diffractometer data at 290 K, ω–2θ scan technique. Mo $K\alpha$ radiation with graphite crystal monochromator. Lattice parameters from least-squares adjustment to setting angles of 25 general reflections [$12 < 2\theta < 20°$ for (2); $40 < 2\theta < 52°$ for (3); $26 < 2\theta < 42°$ for (4)]. Profile analysis on reflection data (Lehmann & Larsen, 1974; Grant & Gabe, 1978). Empirical absorption correction by ψ scans (Phillips & Mathews, 1968), *DIFABS* (Walker & Stuart, 1983). Lorentz and polarization corrections: refinement on F. $\sum w\,|(F_o - F_c|)^2$ minimized, $w = 1/\sigma^2 F_o + g\,F_o^2$; $\sigma^2 F_o$ from counting statistics. Computer programs: *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and *DIRDIF* (Beurskens, Bosman, Doesburg, van den Hark, Prick, Noordik, Beurskens, Gould & Parthasarathi, 1982) for structure solution; *SHELX*76 (Sheldrick, 1976) for refinement and Fourier synthesis.

(2): Crystals by recrystallization from 2-propanol, very thin plates; crystal 0·25 × 0·25 × 0·01 mm used for data collection; systematic absences $h0l$, $h+l = 2n+1$, $0k0$, $k = 2n+1$; space group $P2_1/n$. Intensity data for 5538 reflections (full sphere with $2\theta < 40°$). Scan angle 0·95°. Scan rate variable with time limit of 50 s reflection^{-1}. Two standard reflections every 30 min, no significant crystal decomposition. Absorption correction factors: ψ-scan data, min. transmission 84%, *DIFABS* 0·64–1·40. Laue symmetry-equivalent reflections averaged, $R_{\rm int} = 0{\cdot}057$. 1389 unique reflections, 524 with $I > 2{\cdot}5\sigma(I)$ used in refinement. Structure solution with *MULTAN*. Isotropic refinement to $R = 0{\cdot}144$. H atoms calculated and tied to parent atoms. Additional reduction of variables (necessary because of the very limited number of 'observed' data caused by extremely thin crystal) by treating phenyl ring as rigid group. Anisotropic refinement in two blocks with 118 parameters per block. $R = 0{\cdot}080$, $wR = 0{\cdot}085$ with g (see above) $= 0{\cdot}004$. Max. Δ/σ in final cycle $< 0{\cdot}8$. Final difference map density $< 0{\cdot}20$ e Å^{-3}.

(3): Crystals by recrystallization from n-hexane, piece 0·3 × 0·3 × 0·3 mm cut from larger fragment. Systematic absences $h0l$, $l = 2n+1$, $0k0$, $k = 2n+1$; space group $P2_1/c$. Intensity data for 3376 reflections (full sphere with $2\theta < 50°$), ω–2θ scan technique, scan angle $(0{\cdot}90 + 0{\cdot}347\tan\theta)°$, scan rate variable with max. scan time of 1 min reflection^{-1}. Two standard reflections measured every 30 min, severe crystal decomposition to about 20% of original intensity; smooth correction curve allowed satisfactory correction as reflected in $R_{\rm int}$. Absorption correction factors: ψ-scan data, min. transmission 91%, *DIFABS* 0·64–1·40. Laue symmetry-equivalent reflections averaged, $R_{\rm int} = 0{\cdot}023$. 1519 unique reflections, 987 with $I > 3\sigma(I)$. Structure solution with *DIRDIF* using Br (*DIRDIF* Patterson option) as input. Remaining 11 non-H atoms found as top 11 peaks in *DIRDIF* difference Fourier map. Isotropic refinement to $R = 0{\cdot}091$. H atoms located from difference Fourier synthesis. Final refinement with 987 reflections and 153 parameters. Non-H atoms anisotropic; C—H bond lengths constrained to 1·07 Å. R = 0·048, wR = 0·050 with g (see above) = 0·0003. Max. Δ/σ in final cycle (full matrix) < 0·10. Final difference map density 0·8 e Å^{-3} around Br and < 0·5 e Å^{-3} elsewhere.

(4): Crystal by recrystallization from n-hexane, 0·10 × 0·25 × 0·50 mm; space group $P\bar{1}$. Intensity data for 5444 reflections collected (full sphere up to $2\theta = 50°$), scan angle 0·9°. Scan rate variable with time limit of 80 s reflection^{-1}. Three standard reflections every 30 min. Intensity fluctuations < 2%. Absorption correction factors: ψ-scan data, min. transmission 93%, *DIFABS* 0·77–1·15. Averaging of Laue symmetry-equivalent reflections, $R_{\rm int}$ = 0·013. 2711 unique reflections, 1562 with $I > 3\sigma(I)$ used for refinement. Structure solution with *MULTAN* in default run. Isotropic least-squares refinement to R = 0·062. H atoms from difference Fourier synthesis. Final refinement of 268 parameters, non-H atoms anisotropic, fixed U's for H atoms (0·06 Å^2). R = 0·032, wR = 0·041, with g (see above) = 0·0001. Max. Δ/σ in final cycle (full matrix) < 0·11. Final difference map density < 0·10 e Å^{-3}.

Molecular-mechanics [*MM*2 force field, Allinger–Still (Still, undated)] calculations, using the structure of (4) as starting model, were used to calculate the

Table 1. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic* (*Hamilton,* 1959) *thermal parameters* (Å^2 × 10^3) *for compound* (2)

	x	y	z	$U_{\rm eq}$
C(1)	1459 (30)	3674 (10)	729 (30)	72 (13)
C(2)	3390 (31)	3673 (11)	27 (27)	60 (12)
C(3)	2690 (36)	3137 (11)	−883 (25)	67 (11)
C(4)	1184 (36)	3109 (10)	300 (37)	70 (14)
C(5)	2413 (50)	2725 (14)	1390 (33)	90 (16)
C(6)	4628 (41)	2906 (12)	1302 (22)	83 (17)
C(7)	5039 (32)	3485 (10)	1274 (25)	66 (13)
C(8)	4290 (38)	2726 (9)	−386 (21)	56 (12)
C(9)	3318 (47)	2191 (11)	−433 (40)	95 (17)
C(10)	2324 (51)	2170 (12)	728 (50)	102 (19)
C(11)	105 (17)	4891 (5)	2216 (11)	44 (11)
C(12)	−1569 (17)	4718 (5)	2824 (11)	62 (13)
C(13)	−2571 (13)	5072 (5)	3657 (11)	63 (13)
C(14)	−1899 (17)	5600 (5)	3883 (11)	52 (12)
C(15)	−225 (17)	5773 (5)	3275 (11)	55 (11)
C(16)	777 (17)	5419 (5)	2442 (11)	47 (11)
N(1)	316 (22)	4012 (6)	1313 (21)	60 (10)
N(2)	1075 (25)	4524 (6)	1421 (17)	42 (9)
N(3)	2558 (23)	5635 (8)	1910 (16)	59 (10)
N(4)	−2916 (33)	6006 (10)	4710 (26)	99 (15)
O(1)	3468 (21)	5312 (6)	1141 (15)	70 (8)
O(2)	3017 (24)	6083 (7)	2079 (19)	88 (9)
O(3)	−2327 (27)	6456 (8)	4825 (17)	97 (10)
O(4)	−4333 (25)	5791 (7)	5246 (17)	105 (10)

Table 2. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic* (*Hamilton,* 1959) *thermal parameters* (Å^2 × 10^3) *for compound* (3)

	x	y	z	$U_{\rm eq}$
Br	1038 (1)	2195 (1)	82 (1)	66 (1)
O(1)	3764 (4)	2444 (6)	−2303 (5)	72 (3)
C(1)	2301 (4)	3586 (8)	−544 (5)	40 (2)
C(2)	1922 (4)	3445 (8)	−1776 (5)	36 (2)
C(3)	1015 (5)	5190 (8)	−2068 (5)	41 (2)
C(4)	1765 (5)	6838 (9)	−1394 (6)	48 (2)
C(5)	2330 (5)	5860 (9)	−305 (5)	49 (2)
C(6)	3060 (5)	3794 (9)	−2251 (5)	48 (2)
C(7)	3234 (6)	5882 (9)	−2633 (6)	50 (3)
C(8)	2894 (6)	7486 (9)	−1859 (7)	59 (3)
C(9)	3898 (6)	7615 (10)	−870 (8)	70 (3)
C(10)	3596 (6)	6679 (11)	−46 (7)	66 (3)

Table 3. *Fractional atomic coordinates* (×10^4) *and equivalent isotropic* (*Hamilton,* 1959) *thermal parameters* (Å^2 × 10^2) *for compound* (4)

	x	y	z	$U_{\rm eq}$
C(1)	2810 (4)	1315 (2)	8930 (2)	4·61 (8)
C(2)	4478 (3)	1690 (2)	9854 (2)	4·20 (7)
C(3)	3885 (3)	1335 (2)	10868 (2)	4·62 (8)
C(4)	5394 (3)	1683 (2)	11726 (2)	4·74 (8)
C(5)	7471 (4)	2360 (2)	11614 (2)	4·93 (8)
C(6)	8010 (3)	2704 (2)	10603 (2)	4·56 (8)
C(7)	6560 (3)	2389 (2)	9718 (2)	4·58 (8)
C(8)	2065 (3)	1431 (2)	7072 (2)	4·71 (8)
C(9)	573 (3)	2399 (2)	6910 (2)	4·90 (8)
C(10)	505 (4)	1847 (3)	5693 (2)	5·81 (9)
C(11)	2852 (4)	1702 (2)	5967 (2)	5·30 (9)
C(12)	617 (5)	3049 (3)	5033 (2)	7·75 (12)
C(13)	1721 (3)	3966 (2)	6902 (2)	5·79 (9)
C(14)	2382 (4)	3994 (3)	5730 (2)	7·00 (11)
C(15)	4180 (4)	3219 (3)	5884 (2)	6·01 (9)
C(16)	5278 (4)	3954 (2)	6924 (2)	5·92 (9)
C(17)	3877 (4)	4382 (2)	7522 (2)	5·89 (9)
N(1)	4763 (4)	1331 (2)	12808 (2)	6·61 (9)
N(2)	10215 (3)	3451 (2)	10460 (2)	6·06 (8)
O(1)	967 (2)	812 (2)	9044 (1)	6·79 (7)
O(2)	3618 (2)	1626 (1)	7998 (1)	5·15 (5)
O(3)	2915 (3)	825 (3)	12915 (1)	11·98 (11)
O(4)	6137 (3)	1571 (2)	13540 (1)	8·85 (8)
O(5)	11463 (3)	3716 (2)	11257 (2)	8·63 (8)
O(6)	10670 (3)	3774 (2)	9559 (2)	7·70 (7)

Table 4. *Bond lengths* (Å) *with e.s.d.'s and selected bond angles* (*e.s.d.* 3°) *for* (2)

C(1)—C(2)	1·53 (3)	C(11)—C(12)	1·40 (2)
C(1)—C(4)	1·46 (3)	C(11)—C(16)	1·40 (2)
C(1)—N(1)	1·30 (3)	C(12)—C(13)	1·40 (2)
C(2)—C(3)	1·60 (4)	C(11)—N(2)	1·38 (2)
C(2)—C(7)	1·52 (3)	C(13)—C(14)	1·40 (2)
C(3)—C(4)	1·58 (4)	C(14)—C(15)	1·40 (2)
C(3)—C(8)	1·50 (3)	C(14)—N(4)	1·48 (3)
C(4)—C(5)	1·51 (4)	C(15)—C(16)	1·40 (2)
C(5)—C(6)	1·57 (5)	C(16)—N(3)	1·46 (2)
C(5)—C(10)	1·50 (5)	N(1)—N(2)	1·37 (2)
C(6)—C(7)	1·47 (4)	N(3)—O(1)	1·27 (2)
C(6)—C(8)	1·55 (3)	N(3)—O(2)	1·16 (3)
C(8)—C(9)	1·48 (4)	N(4)—O(3)	1·19 (3)
C(9)—C(10)	1·32 (5)	N(4)—O(4)	1·25 (3)

C—H distances 1·08 (2) Å, constrained

C(2)—C(1)—C(4)	88	C(4)—C(5)—C(6)	103
C(2)—C(1)—N(1)	139	C(4)—C(5)—C(10)	110
C(4)—C(1)—N(1)	132	C(6)—C(5)—C(10)	103
C(1)—C(2)—C(3)	90	C(5)—C(6)—C(7)	118
C(1)—C(2)—C(7)	106	C(5)—C(6)—C(8)	88
C(3)—C(2)—C(7)	104	C(7)—C(6)—C(8)	106
C(2)—C(3)—C(4)	82	C(2)—C(7)—C(6)	102
C(2)—C(3)—C(8)	106	C(3)—C(8)—C(6)	95
C(4)—C(3)—C(8)	106	C(3)—C(8)—C(9)	108
C(1)—C(4)—C(3)	94	C(6)—C(8)—C(9)	107
C(1)—C(4)—C(5)	114	C(8)—C(9)—C(10)	107
C(3)—C(4)—C(5)	96	C(5)—C(10)—C(9)	106

structure of (1) and particularly the distances between the atoms of the C=C and C=O bonds. Atomic scattering factors from *SHELX*.*

Discussion. Atomic coordinates are given in Tables 1 (2), 2 (3) and 3 (4). Molecular geometry data are collected in Tables 4 through 6. The crystallographic atomic numbering schemes are given in Fig. 1. Stereoviews of the molecules showing the atomic connectivity of the cage skeleton are presented in Fig. 2. Fig. 1 shows the differences in atomic connectivity in the cage skeletons of (2), (3) and (4). Only (4) has the original cage structure of (1). The formation of (2) from (1) can be explained by the acid-catalyzed cyclobutyl/

Table 5. *Bond lengths* (Å) *with e.s.d.'s and bond angles* (*e.s.d.* 0·5°) *for* (3)

Br–C(1)	1·979 (5)	C(4)–C(5)	1·532 (9)
C(1)–C(5)	1·541 (8)	C(6)–C(7)	1·497 (8)
C(3)–C(4)	1·522 (8)	C(9)–C(10)	1·319 (12)
C(5)–C(10)	1·475 (9)	C(1)–C(2)	1·529 (8)
C(8)–C(9)	1·489 (12)	C(2)–C(6)	1·527 (7)
O(1)–C(6)	1·200 (7)	C(4)–C(8)	1·554 (9)
C(2)–C(3)	1·529 (7)	C(7)–C(8)	1·549 (9)

C–H distances 1·07 (1) Å, constrained

Br–C(1)–C(2)	108·5	C(1)–C(5)–C(10)	112·6
Br–C(1)–C(5)	111·5	C(4)–C(5)–C(10)	103·3
C(2)–C(1)–C(5)	104·5	O(1)–C(6)–C(2)	120·7
C(1)–C(2)–C(3)	102·9	O(1)–C(6)–C(7)	123·0
C(1)–C(2)–C(6)	108·9	C(2)–C(6)–C(7)	116·3
C(3)–C(2)–C(6)	110·2	C(6)–C(7)–C(8)	111·6
C(2)–C(3)–C(4)	99·1	C(4)–C(8)–C(7)	112·0
C(3)–C(4)–C(5)	105·6	C(4)–C(8)–C(9)	102·4
C(3)–C(4)–C(8)	112·0	C(7)–C(8)–C(9)	109·5
C(5)–C(4)–C(8)	104·5	C(8)–C(9)–C(10)	111·6
C(1)–C(5)–C(4)	104·6	C(5)–C(10)–C(9)	112·9

Table 6. *Bond lengths* (Å) *with e.s.d.'s and selected bond angles* (*e.s.d.* 0·2°) *for* (4)

C(1)–C(2)	1·501 (3)	C(9)–C(13)	1·566 (3)
C(1)–O(1)	1·199 (2)	C(10)–C(11)	1·571 (3)
C(1)–O(2)	1·325 (2)	C(10)–C(12)	1·494 (4)
C(2)–C(3)	1·388 (3)	C(11)–C(15)	1·570 (3)
C(2)–C(7)	1·388 (3)	C(12)–C(14)	1·491 (4)
C(3)–C(4)	1·377 (3)	C(13)–C(14)	1·539 (4)
C(4)–C(5)	1·374 (3)	C(13)–C(17)	1·511 (3)
C(4)–N(1)	1·472 (3)	C(14)–C(15)	1·536 (4)
C(5)–C(6)	1·372 (3)	C(15)–C(16)	1·497 (3)
C(6)–C(7)	1·378 (3)	C(16)–C(17)	1·312 (3)
C(6)–N(2)	1·473 (3)	N(1)–O(3)	1·201 (3)
C(8)–C(9)	1·518 (3)	N(1)–O(4)	1·211 (2)
C(8)–C(11)	1·512 (3)	N(2)–O(5)	1·220 (2)
C(8)–O(2)	1·462 (2)	N(2)–O(6)	1·223 (2)
C(9)–C(10)	1·564 (3)		

C–H distances 0·90–0·99 (2) Å

C(9)–C(8)–C(11)	88·6	C(10)–C(12)–C(14)	94·8
C(9)–C(8)–O(2)	122·9	C(9)–C(13)–C(14)	100·9
C(11)–C(8)–O(2)	119·3	C(9)–C(13)–C(17)	114·7
C(8)–C(9)–C(10)	84·1	C(14)–C(13)–C(17)	101·1
C(8)–C(9)–C(13)	114·6	C(12)–C(14)–C(13)	107·4
C(10)–C(9)–C(13)	102·2	C(12)–C(14)–C(15)	107·7
C(9)–C(10)–C(11)	84·9	C(13)–C(14)–C(15)	95·7
C(9)–C(10)–C(12)	108·1	C(11)–C(15)–C(14)	101·0
C(11)–C(10)–C(12)	108·0	C(11)–C(15)–C(16)	114·9
C(8)–C(11)–C(10)	84·1	C(14)–C(15)–C(16)	100·8
C(8)–C(11)–C(15)	114·6	C(15)–C(16)–C(17)	109·5
C(10)–C(11)–C(15)	102·0	C(13)–C(17)–C(16)	108·1

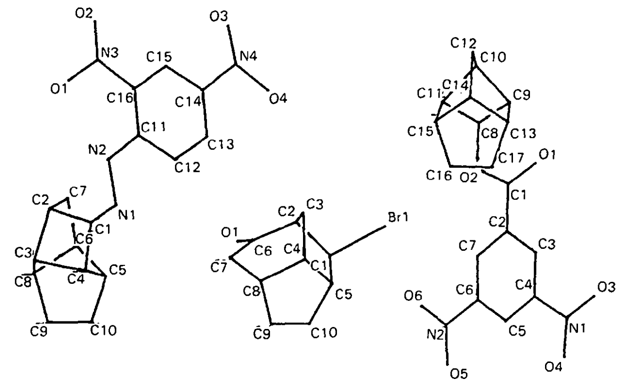


Fig. 1. Crystallographic atomic numbering. H atoms (omitted for clarity) are numbered according to parent atoms. Left (2), centre (3), right (4).

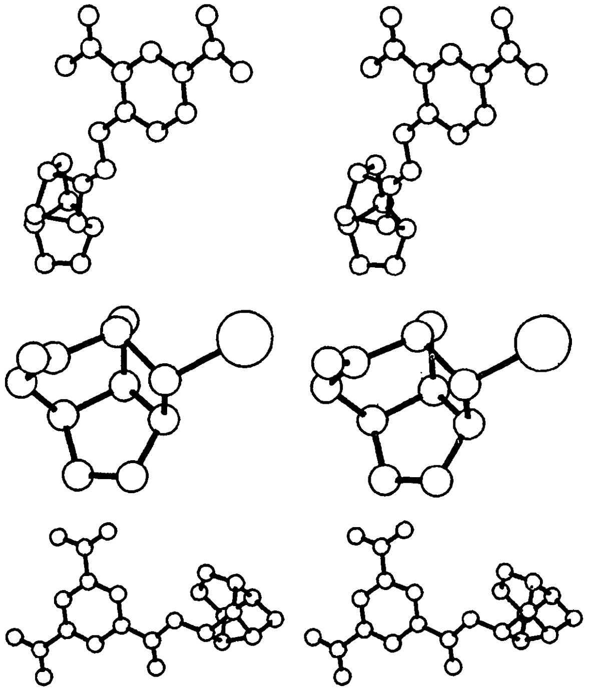


Fig. 2. Stereoviews of the molecules (H atoms omitted) with emphasis on cage structure. Top (2), middle (3), bottom (4). Note the short C8–(C16,C17) distance in (4).

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* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42381 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

cyclopropyl carbinyl carbocation rearrangement (Sakkers, Vankan, Klunder & Zwanenburg, 1979). Such a rearrangement reaction is also observed when (1) is treated with HCl or HBr in methanol, resulting in (3). The initially formed cyclopropyl cation, in this case, reacts rapidly with the bromide anion. In the absence of such a strong nucleophile, further bond reorganization leads to the tetracyclo[4.4.0.0^{2,8}.0^{4,7}]dec-9-en-5-one system (2). (4) has the molecular structure anticipated for (1) and shows the *endo* configuration of the dinitrophenyl ester function. Bond distances and angles are all in the range expected for these strained structures and no intermolecular distances significantly shorter than expected from van der Waals contacts are observed.

In (4), the distance between C(8) and the olefinic carbon atoms C(16) and C(17) is 2·90 Å. The molecular-mechanics calculation on (1) gives values of 2·70 and 3·34 Å respectively for the distance between the carbonyl carbon and the olefinic bond and the carbonyl oxygen atom and the olefinic bond. These distances indicate an interaction between the two double bonds in compound (1) as suggested by its UV spectrum.

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Dipyridinium Oxalate–Oxalic Acid

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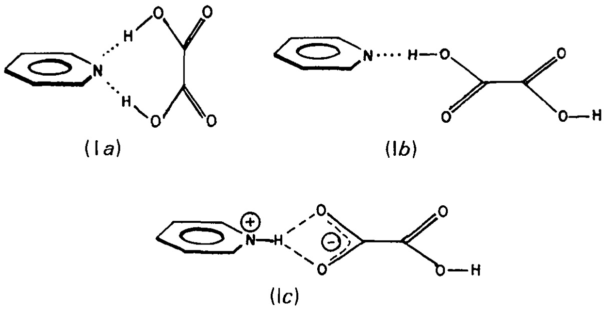
Abstract. $2C_5H_6N^+.C_2O_4^{2-}.C_2H_2O_4$, $M_r = 338\cdot3$, triclinic, $P\bar{1}$, $a = 3\cdot999$ (2), $b = 8\cdot439$ (4), $c = 11\cdot319$ (3) Å, $\alpha = 77\cdot96$ (3), $\beta = 88\cdot64$ (2), $\gamma = 82\cdot69$ (3)°, $V = 370\cdot5$ (4) Å^3, $Z = 1$, $D_x = 1\cdot516$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0\cdot71073$ Å, $\mu = 1\cdot18$ cm^{-1}, $F(000) = 176$, $T = 301$ K, $R = 0\cdot041$ for 1390 observations (of 2155 unique data). The title structure consists of two pyridinium ions hydrogen bonded to one oxalate ion, which lies on a center of symmetry. An additional centrosymmetric oxalic acid molecule forms hydrogen bonds with the oxalate moiety to give linear chains along the *c* axis.

Introduction. A 1:1 adduct between pyridine and oxalic acid was first reported in a solubility study (Grigorowsky & Kimen, 1945). Considering the reduced acidity of the second proton of oxalic acid, an equimolar mixture of pyridine and oxalic acid would be expected to give a pyridinium hydrogen oxalate species (pyridinium = pK_a 5·25; oxalic acid = pK_a 1·23, 4·19). Three possible interactions of a 1:1 adduct, as depicted in the scheme below, are: a μ-bonded pyridine to both acidic protons (I*a*) or pyridine interacting with one acidic proton in either of two fashions (I*b* or I*c*). In search of further examples of a pyridine μ-bonding to two atoms (I*a*) (Newkome, Lee & Fronczek, 1985), structure determination of the pyridine–oxalic acid adduct was undertaken.



(I*a*) (I*b*)

(I*c*)

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