$[\sigma^2(F_o) + (0{\cdot}03F)^2]^{-1}$; max. (Δ/σ) 0·32; final $R = 0{\cdot}047$ and $wR = 0{\cdot}051$, $S = 0{\cdot}64$; $\Delta\rho$ excursions in final difference map 0·3 e Å^{-3}; atomic scattering factors from *International Tables for X-ray Crystallography* (1974); calculations carried out on HITAC M-280 computer at the Computer Center of the University of Tokyo. The final atomic parameters for non-H atoms are in Table 1.* A projection of the structure along the *c* axis is shown in Fig. 1, and a perspective drawing of the molecule with the numbering scheme is shown in Fig. 2. The bond lengths and angles are listed in Table 2.

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* Lists of the structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, and equations of mean planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43876 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of 13,13-Dimethyl-1,2-didehydrocrotalanine Picrate: A Pyrrolizidine Alkaloid Analogue

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Abstract. $C_{15}H_{22}NO_4^+.C_6H_2N_3O_7^-$, $M_r = 508{\cdot}4$, monoclinic, $P2_1$, $a = 12{\cdot}714\ (1)$, $b = 6{\cdot}754\ (3)$, $c = 14{\cdot}504\ (1)$ Å, $\beta = 103{\cdot}97\ (1)°$, $V = 1208{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}397$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}11$ mm^{-1}, $F(000) = 532$, $T = 293\ (1)$ K, $R = 0{\cdot}085$ for 1579 reflections. The ester carbonyl bonds in the 11-membered macrocyclic pyrrolizidine alkaloid analogue are antiparallel and the pyrrolizidine nucleus has an *exo* conformation. The picrate ion and the alkaloid analogue are linked through the phenolic O atom, O(7), of the picrate and the N atom, N(4), of the alkaloid analogue [O(7)···N(4) 2·62 (1), O(7)···H(4) 1·73 (1) Å; N(4)—H(4)···O(7) 136 (1)°].

Experimental. Yellow rod-like crystals grown from EtOH/MeOH, dimensions 0·08 × 0·11 × 0·46 mm. Stoe–Siemens AED four-circle diffractometer, monochromated Mo $K\alpha$ radiation, ω/θ scan mode, $2\theta_{\max} = 50°$, $\pm h\ {+k}\ {+l}$, four check reflections with no intensity change, 2277 unique reflections of which 1586 with $F > 3\sigma(F)$ used for all calculations, program system *SHELX76* (Sheldrick, 1976). Index ranges $|h| \leq 14$, $k\ 0\to 8$, $l\ 0\to 17$. Cell constants refined from $\pm\omega$ values of ten reflections and their equivalents in the range $30 < 2\theta < 40°$. No absorption or extinction corrections applied. Structure solution using the *DIRDIF* system (Beurskens *et al.*, 1984) (after introducing coordinates for a picrate ion followed by the use of the programs *ORIENT, TRADIR* and *DIRDIF*). Blocked full-matrix least-squares refinement to $R = 0{\cdot}085$, $wR = 0{\cdot}081$ for 1579 reflections (seven reflections probably suffering from extinction removed), all non-H atoms anisotropic, phenyl group as rigid hexagon (C—C 1·395 Å), H atoms included using a riding model [C—H 1·08, N—H 1·01 Å, overall $U(\mathrm{H})_{\mathrm{iso}}$ refined, benzene type 0·081, CH_2 type 0·072, CH_3 type 0·098 Å^2], 326 parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0{\cdot}0023F^2$ which gave a featureless analysis of variance, max. $(\Delta/\sigma) = 0{\cdot}85$, ave. $(\Delta/\sigma) < 0{\cdot}2$, max. and min. heights in the final $\Delta\rho$ map 0·33 and −0·40 e Å^{-3}, respectively. Origin definition implicit in blocked refinement. The probable cause of the relatively high R indices was the small crystal (for Mo $K\alpha$ radiation), hence the low reflection:parameter ratio (4·8). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The atomic

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Table 1. *Final positional and equivalent isotropic thermal parameters* (× 10^4)

$$U_{eq} = \tfrac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}(Å^2)
Picrate ion				
C(1)	907 (3)	19 (10)	1100 (2)	487 (23)
C(2)	771 (3)	−15 (10)	116 (2)	433 (21)
C(3)	−269 (3)	−22 (10)	−481 (2)	440 (20)
C(4)	−1173 (3)	5 (10)	−95 (2)	456 (21)
C(5)	−1037 (3)	39 (10)	889 (2)	428 (21)
C(6)	3 (3)	46 (10)	1486 (2)	465 (21)
O(7)	1850 (4)	−65 (13)	1698 (4)	546 (18)
N(8)	1671 (6)	12 (13)	−339 (6)	881 (26)
O(9)	2567 (5)	−557 (13)	129 (5)	577 (20)
O(10)	1495 (6)	540 (14)	−1164 (5)	668 (23)
N(11)	−2257 (5)	−80 (11)	−703 (6)	816 (23)
O(12)	−3020 (4)	−293 (11)	−328 (4)	451 (17)
O(13)	−2351 (5)	135 (13)	−1574 (4)	535 (19)
N(14)	118 (7)	254 (22)	2502 (5)	1144 (32)
O(15)	615 (8)	1633 (22)	2898 (6)	1144 (35)
O(16)	−354 (9)	−998 (18)	2880 (6)	1003 (35)
Cation				
C(1)	5252 (6)	1024 (14)	1535 (5)	404 (23)
C(2)	5465 (7)	−882 (15)	1512 (6)	489 (25)
C(3)	4695 (7)	−2131 (15)	1892 (7)	562 (27)
N(4)	3952 (5)	−624 (11)	2180 (4)	704 (20)
C(5)	3921 (7)	−686 (15)	3210 (6)	584 (27)
C(6)	3768 (7)	1501 (15)	3430 (6)	523 (26)
C(7)	4494 (6)	2511 (13)	2915 (5)	394 (21)
C(8)	4329 (6)	1410 (12)	1975 (6)	375 (21)
C(9)	5804 (7)	2643 (14)	1108 (6)	525 (25)
O(10)	6249 (4)	4160 (9)	1801 (4)	232 (13)
C(11)	7241 (7)	3715 (17)	2378 (6)	565 (28)
C(12)	7596 (7)	5442 (15)	3050 (6)	555 (26)
C(13)	7984 (6)	4946 (18)	4110 (6)	580 (24)
C(14)	7272 (7)	3350 (17)	4421 (6)	611 (27)
C(15)	6039 (7)	3742 (18)	4039 (6)	598 (29)
O(16)	5622 (4)	2294 (10)	3412 (3)	258 (14)
O(17)	5540 (5)	5087 (15)	4228 (5)	566 (21)
O(18)	7704 (5)	2211 (12)	2339 (5)	489 (20)
C(19)	9133 (7)	4140 (22)	4319 (8)	840 (35)
C(20)	8002 (8)	6884 (19)	4678 (7)	787 (33)

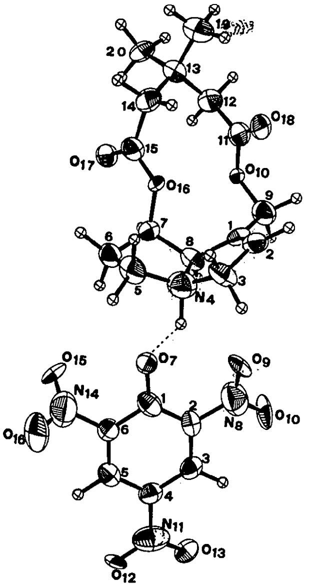

Fig. 1. View of the molecule showing the numbering scheme and vibrational ellipsoids (50% probability level).

parameters are given in Table 1,* bond lengths and angles in Table 2. Selected torsion angles in the alkaloid analogue are given in Table 3. Fig. 1, drawn using *ORTEP*II (Johnson, 1976), shows the molecule and the numbering scheme.

Table 2. *Distances* (Å) *and angles* (°) *in the cation*

C(1)–C(2)	1·317 (14)	C(9)–O(10)	1·451 (10)
C(1)–C(9)	1·511 (13)	O(10)–C(11)	1·368 (10)
C(1)–C(8)	1·488 (12)	C(11)–C(12)	1·517 (14)
C(2)–C(3)	1·494 (14)	C(11)–O(18)	1·182 (14)
C(3)–N(4)	1·514 (12)	C(12)–C(13)	1·533 (12)
N(4)–C(5)	1·505 (12)	C(13)–C(14)	1·544 (15)
N(4)–C(8)	1·508 (11)	C(13)–C(19)	1·520 (13)
C(5)–C(6)	1·533 (14)	C(13)–C(20)	1·543 (16)
C(6)–C(7)	1·486 (13)	C(14)–C(15)	1·554 (12)
C(7)–C(8)	1·522 (11)	C(15)–O(16)	1·354 (12)
C(7)–O(16)	1·449 (8)	C(15)–O(17)	1·177 (14)
C(8)–C(1)–C(2)	111·7 (8)	C(9)–O(10)–C(11)	114·6 (7)
C(9)–C(1)–C(2)	125·3 (8)	O(10)–C(11)–C(12)	108·2 (8)
C(8)–C(1)–C(9)	122·8 (8)	O(10)–C(11)–O(18)	123·8 (9)
C(1)–C(2)–C(3)	112·7 (8)	C(12)–C(11)–O(18)	128·0 (8)
C(2)–C(3)–N(4)	103·3 (8)	C(11)–C(12)–C(13)	116·8 (8)
C(3)–N(4)–C(5)	115·0 (7)	C(12)–C(13)–C(14)	112·1 (7)
C(3)–N(4)–C(8)	108·0 (7)	C(12)–C(13)–C(19)	109·8 (8)
C(8)–N(4)–C(5)	107·8 (7)	C(12)–C(13)–C(20)	108·0 (9)
N(4)–C(5)–C(6)	102·4 (7)	C(14)–C(13)–C(19)	107·1 (9)
C(5)–C(6)–C(7)	102·2 (8)	C(14)–C(13)–C(20)	111·8 (8)
C(6)–C(7)–C(8)	105·0 (7)	C(19)–C(13)–C(20)	107·9 (8)
C(6)–C(7)–O(16)	111·3 (6)	C(13)–C(14)–C(15)	112·9 (8)
C(8)–C(7)–O(16)	107·6 (6)	C(14)–C(15)–O(16)	108·2 (8)
C(7)–C(8)–C(1)	121·2 (6)	C(14)–C(15)–O(17)	127·0 (9)
C(7)–C(8)–N(4)	104·5 (7)	O(16)–C(15)–O(17)	124·7 (8)
C(1)–C(8)–N(4)	104·2 (7)	C(15)–O(16)–C(7)	116·2 (7)
C(1)–C(9)–O(10)	111·6 (7)		

Table 3. *Selected torsion angles* (°) *in the pyrrolizidine alkaloid analogue* (*e.s.d.'s ca* 1·5° *in the title compound*)

	Title compound	1,2-Didehydro-crotalanine*
C(8)–C(1)–C(9)–O(10)	58·8	63·1
C(1)–C(9)–O(10)–C(11)	82·3	79·6
C(9)–O(10)–C(11)–C(12)	179·5	−175·8
O(10)–C(11)–C(12)–C(13)	130·1	134·7
C(11)–C(12)–C(13)–C(14)	−41·1	−52·1
C(12)–C(13)–C(14)–C(15)	−46·0	−33·9
C(13)–C(14)–C(15)–O(16)	113·5	106·4
C(14)–C(15)–O(16)–C(7)	−174·7	−175·6
C(15)–O(16)–C(7)–C(8)	154·0	157·0
O(16)–C(7)–C(8)–C(1)	−23·3	−21·6
C(7)–C(8)–C(1)–C(9)	−70·3	−75·9
H(9a)–C(9)–C(1)–C(2)	114·4	−7·5
H(9b)–C(9)–C(1)–C(2)	−5·0	112·4
H(9a)–C(9)–O(10)–C(11)	−158·1	−40·7
H(9b)–C(9)–O(10)–C(11)	−38·7	−160·4
C(9)–O(10)–C(11)–O(18)	−1·3	0·5
$\Delta\delta$(H9) (p.p.m.)*	1·24	0·62
Angle between carbonyl bonds (°)	163·7	164·5

* Devlin, Robins & Sakdarat (1982).

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* Lists of structure factors, bond distances and angles in the picrate ion, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43922 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Related literature. The title compound was prepared from (+)-retronecine and 3,3-dimethylglutaric anhydride (Devlin, Robins & Sakdarat, 1982). Because the absolute configuration of (+)-retronecine is known (Bull, Culvenor & Dick, 1968; Warren, 1966), Fig. 1 and the coordinates (Table 1) correspond to the absolute configuration of the title compound. The geometry and conformation of the molecule (Table 3) are very close to those observed in the first pyrrolizidine alkaloid analogue studied, 1,2-didehydrocrotalanine picrate (Stoeckli-Evans & Robins, 1983). The latter was prepared from (+)-retronecine and glutaric anhydride (Devlin, Robins & Sakdarat, 1982). The ^{1}H NMR chemical shift difference [$\Delta\delta$] of the C(9) H atoms is quite different for the two compounds despite the same relative orientation of the C(9) H atoms with respect to bonds C(1)=C(2) and O(10)—C(11); see Table 3.

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trans-Decafluoroazobenzene–*trans*-Stilbene (1/1)

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Abstract. $C_{12}F_{10}N_2.C_{14}H_{12}$, $M_r = 542·4$, triclinic, $P\bar{1}$, $a = 6·167\ (1)$, $b = 7·365\ (1)$, $c = 12·394\ (2)$ Å, $\alpha = 98·39\ (1)$, $\beta = 92·01\ (1)$, $\gamma = 94·52\ (2)°$, $V = 555\ (1)$ Å^3, $D_m = 1·63\ (1)$, $D_x = 1·623$ Mg m^{-3}, $Z = 1$, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, $\mu = 0·107$ mm^{-1}, $F(000) = 272$, $T = 293\ (2)$ K, $R = 0·040$ for 1041 reflections with $I \geq 2·5\sigma(I)$. The crystal structure of the title compound is comprised of alternate (almost parallel, 3·7°) layers of decafluoroazobenzene molecules and stilbene molecules with the individual molecules situated about crystallographic centres of inversion. The molecules are stacked along the b axis, forming columns, but are not eclipsed; the average interlayer spacing is 3·55 Å. The shortest F···H contact in the lattice is an inter-column contact between F(4) and H(7′) (1+x, y, z−1) of 2·70 Å. Within the layers of decafluoroazobenzene, the closest intermolecular contact occurs between F(2) and F(2′) (−x, −1−y, −z) of 3·04 Å; similarly, H(4)···H(6′) (1+x, y, z) contacts of 2·95 Å are found within the layers of stilbene molecules.

Experimental. Orange crystals of the 1/1 molecular complex between decafluoroazobenzene and stilbene (*trans*-1,2-diphenylethene), m.p. 428–430 K, were originally obtained as the only isolable product from a reaction between the azo compound and Pt(η^2-CHPh=CHPh)(PEt$_3$)$_2$. The title compound was subsequently prepared directly from the two components in CCl$_4$ solution. Analysis: found C, 57·2; H, 2·2; N, 5·5; $C_{26}H_{12}F_{10}N_2$ calc. C, 57·6; H, 2·2; N, 5·2%. Crystals suitable for the X-ray analysis were obtained from the slow evaporation of a CCl$_4$ solution. Density measured in aq. ZnBr$_2$ solution. Enraf–Nonius CAD-4F diffractometer controlled by a PDP8/A computer, graphite-monochromated Mo $K\bar{\alpha}$ radiation; ω:2θ scan technique. Cell parameters, on a needle 0·138 × 0·475 × 0·025 mm, from least-squares procedure on 25 reflections ($8 \leq \theta \leq 13°$). Total of 4570 reflections ($1 \leq \theta \leq 27·5°$) measured in the range $-8 \leq h \leq 8$, $-9 \leq k \leq 9$, $-16 \leq l \leq 9$. A decrease of approximately 8% was noted in the net intensities of

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