116. Structures of Ring-Enlargement Products

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Crystal structures have been determined of methyl *trans*-1-hydroxy-6-nitro-3-oxobicyclo[4.4.0]decane-2-carboxylate (19), *cis*-3-methyl-6-nitro-2-oxabicyclo[4.4.0]decan-1-ol (2), *cis*-7-hydroxy-1-nitrobicyclo[5.4.0]undecan-9-one (13), and the medium-ring compounds 2-acetyl-4-nitrocyclooctanone (9), methyl 5-nitro-2-oxocyclooctanecarboxylate (4), 2-acetyl-4-nitrocyclononanone (11), 2-acetyl-4-nitrocyclodecanone (15), benzyl 5-nitro-2,11-dioxocycloundecanecarboxylate (24), methyl 5-nitro-2,12-dioxocyclododecanecarboxylate (21), and 8-nitro-11-oxo-13-tridecanolide (7), which are intermediates, side products, or end products of the 'Zip' ring-enlargement reaction. The conformations of most of the medium-ring compounds are very similar to equal-sized ring compounds previously determined by other authors.

In the past, a new method for ring enlargement by the so-called 'Zip' reaction was developed by which a number of new polyaminolactams were synthesized starting from lactams [1]. The same reaction principle was followed to convert carbocyclic compounds
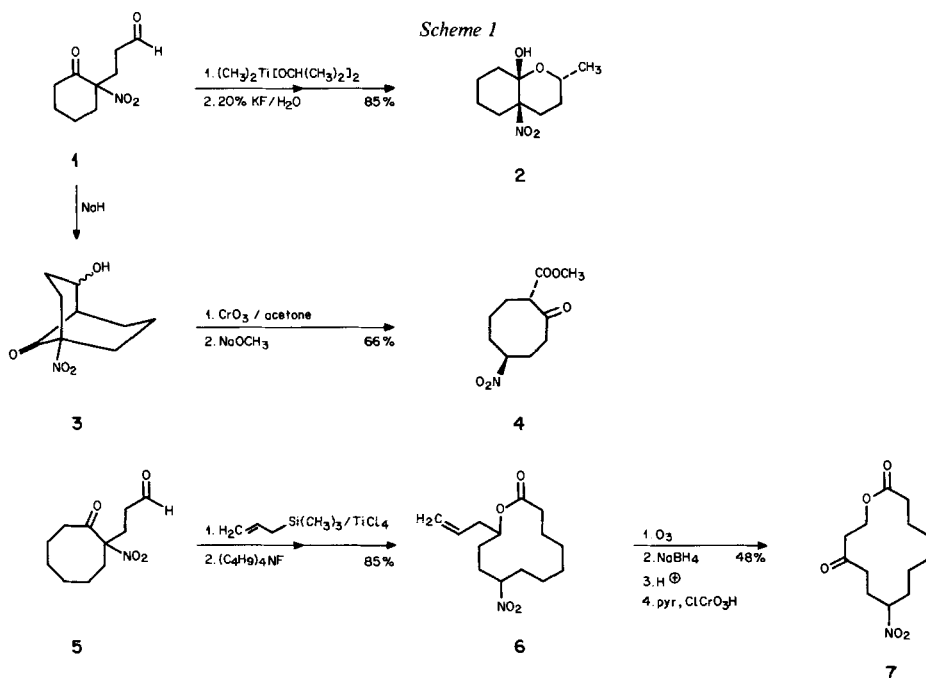
Scheme 1

to pharmacologically important lactones with medium or large rings. 3-(1-Nitro-2-oxo-cyclohexyl)propanal (**1**) (prepared from 2-nitrocyclohexanone and acrylaldehyde [2]) gave, stereospecifically, bicyclic lactone **2** in 85% yield by treatment with $(CH_3)_2Ti[OCH(CH_3)_2]_2$ *(Scheme 1)* [3]. An internal aldol-type reaction of **1** led to **3** which was then oxidized to the corresponding ketone and converted by ring opening to the eight-membered ring compound **4** using $NaOCH_3/CH_3OH$ [4]. A two-step ring enlarge-ment was necessary to convert the eight-membered ring of **5** *via* the twelve-membered ring intermediate **6** to the fourteen-membered ring product **7** [5] *(Scheme 1)*. A further variation of this ring-enlargement method is provided by the transformation of carbocy-clic compounds to lactams [6]. Finally, it is possible to enlarge carbocyclic to extended carbocyclic compounds by incorporation of a C chain attached to the smaller ring into the larger ring [7] [8].

In most of the cases mentioned above, the incorporation of a C_4 moiety takes place in one step. Treatment of 2-nitro-2-(3'-oxobutyl)cyclohexanone (**8**), prepared by the *Mi-chael* reaction of 2-nitrocyclohexanone and methyl vinyl ketone, yielded (in the presence of *t*-BuOK/THF at −80°) the eight-membered 2-acetyl-4-nitrocyclooctanone (**9**) *(Scheme 2)*. Unfourtunately, under the same conditions compounds **10** and **14**, homo-logs of **8**, are converted to mixtures. For example, treatment of the seven-membered **10** led to a mixture of nine-membered **11** and eleven-membered **12**. Furthermore, the bicyclic intermediate *cis*-7-hydroxy-1-nitrobicyclo[5.4.0]undecan-9-one (**13**) was formed in small amounts. Compound **13** was converted to **12** using base catalysis. Therefore, formation of **12** takes place by opening of the six-membered-ring moiety of the bicyclic intermediate, in which the NO_2 and the OH groups are *cis* to each other. On the other hand, ring-en-

Scheme 2

8   9

10   11 44%   12 35%   13 7%

14   15 5%   16 40%   17 25%
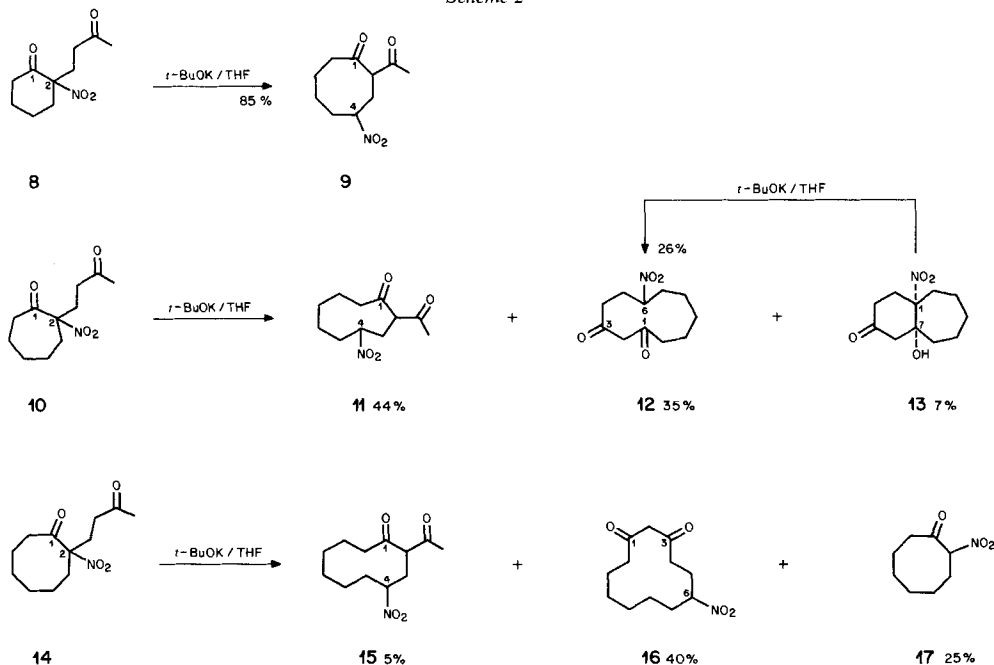
Scheme 3
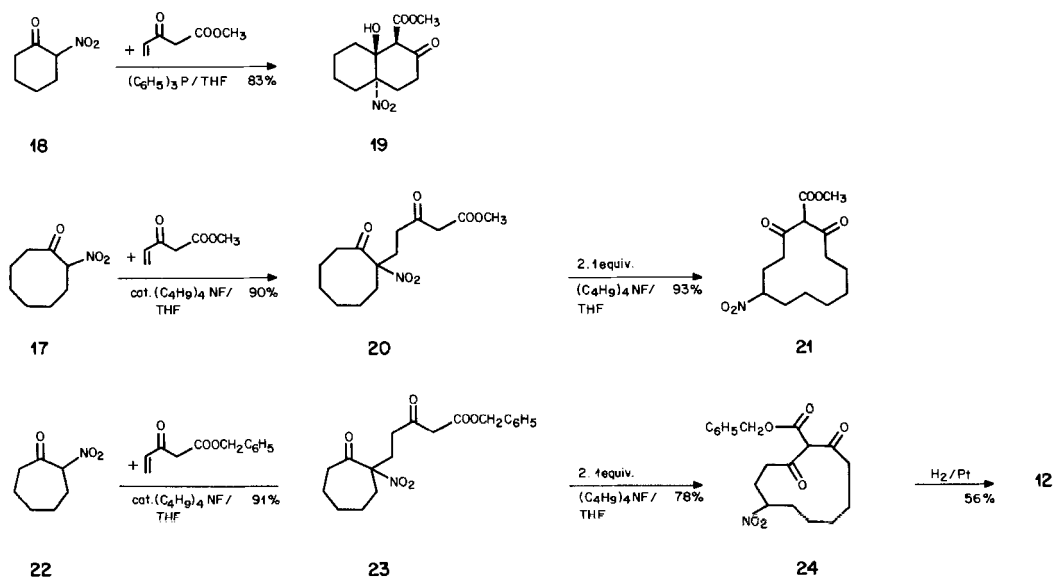
largement product **11** was formed *via* a similar, but four-membered-ring-containing intermediate. Under similar conditions, eight-membered **14** forms the *retro-Michael* product **17** in addition to the corresponding ring-enlargement products **15** and **16**. The *Michael* acceptors methyl or benzyl 3-oxo-4-pentenoate [9] were used instead of methyl vinyl ketone to eliminate the uncertainty in product formation (*e.g.* ring-enlargement products *via* four- and six-membered ring intermediates *vs.* intermediates themselves). The ring-enlargement products *via* a six-membered intermediate were formed in high yield except by the reaction of 2-nitrocyclohexanone (**18**). 2-Nitrocyclooctanone (**17**) yielded methyl 5-nitro-2,12-dioxocyclododecan-1-carboxylate (**21**) *via* methyl 3-oxo-5-(1-nitro-2-oxocyclooctyl)pentanoate (**20**) in 84% and 2-nitrocycloheptanone (**22**) yielded benzyl 5-nitro-2,11-dioxocycloundecane-1-carboxylate (**24**) *via* benzyl 3-oxo-5-(1-nitro-2-oxocycloheptyl)pentanoate (**23**) in 71%. Compound **18** gave methyl *trans*-1-hydroxy-6-nitro-3-oxobicyclo[4.4.0]decane-2-carboxylate (**19**) which cannot undergo a ring enlargement because of the *trans*-arrangement of the OH and the NO$_2$ group *(Scheme 3)*. Hydrolysis followed by decarboxylation of compounds of type **21** was not possible. However, hydrogenolysis and decarboxylation of those of type **24** led to 1,3-diketones of type **12**.

The differentiation of the non-rearranged and rearranged products given in *Schemes 1–3* was achieved by TLC and spectral data. However, in most cases it was not possible to get independent structure proofs by spectra (IR, ¹H-, ¹³C-NMR and MS). Accurate molecular-weight determination was accomplished by electron-impact mass spectroscopy (EI-MS; **4, 9, 11, 13**) or by chemical-ionization mass spectra (CI-MS, 2-methyl-propane as reactant gas, **2** and **7**). In all cases, it was not possible to establish the structures by fragment-ion formation. Besides the known fragmentation pattern of the nitro group on an aliphatic chain ([M-46] or [M-30] *etc.*) and other functional groups, no characteristic fragmentation patterns can be detected. The analysis of the complex ¹H- and ¹³C-NMR spectra (CDCl₃) of the products turned out to be rather difficult because of

Table 1.

Compound[a])	19	2	13	9′
Solvent system for crystallization	EtOAc/Et$_2$O/hexane	CH$_2$Cl$_2$/hexane	EtOAc/Et$_2$O/pentane	EtOAc/pentane
Formula	C$_{12}$H$_{17}$NO$_6$	C$_{10}$H$_{17}$NO$_4$	C$_{11}$H$_{17}$NO$_4$	C$_{10}$H$_{15}$NO$_4$
Formula weight	271.29	215.25	227.26	213.23
Temp. *(ca.)* [K]	130	130	295	130
Space group	$P2_1/c$	$Pbca$	$P2_1/c$	$P2_1/c$
Z	4	8	4	4
a [Å]	13.318(2)	6.522(1)	8.708(1)	9.278(1)
b [Å]	6.412(1)	15.100(2)	11.540(1)	9.210(1)
c [Å]	14.913(1)	20.921(3)	12.585(1)	11.890(1)
β [°]	103.56(1)	90	112.77(1)	97.88(1)
No. of reflections centered	120	96	64	50
Range [°]	$35 < |2\Theta| < 47$	$41 < |2\Theta| < 50$	$28 < |2\Theta| < 34$	$36 < |2\Theta| < 46$
D_x [g/cm^3]	1.46	1.39	1.29	1.41
$2\Theta_{max}$ [°]	60	60	60	74
No. of unique reflections	3595	3014	3397	5116
No. of variables	240	204	209	196
R	0.054	0.053	0.091	0.065
R_w	0.049	0.045	0.086	0.056
Rec. weighting scheme[b]), $1/w$	$\sigma_F^2 + 0.0003F^2$	$\sigma_F^2 + 0.0003F^2$	$\sigma_F^2 + 0.0006F^2$	$\sigma_F^2 + 0.0006F^2$

[a]) The meaning of primes in some of the compound numbers is defined below.

many similar structural elements and diastereomer and keto-enol mixtures; *e.g.* **21** exists in CDCl$_3$ solution at 25° at least in four different isomers; for the 14 C-atoms of the molecule 52 ^{13}C-absorptions were registered in the spectrum [8].

To establish their structures including their relative configuration, the important compounds in each series had to be analyzed by a different method. Therefore, X-ray diffraction analyses of **2, 4, 7, 9, 11, 13, 15, 19, 21**, and **24** were performed to establish or confirm the structures and to examine their bonding geometries for signs of the effects of steric interaction or conformational properties that might provide insight into the chemical properties of these ring compounds (see *Table 1*).

The intensities were collected on a *Nicolet-R3* diffractometer in the ω-scan mode using MoK_α radiation and the usual corrections except for absorption were applied. For those reflections whose intensities I were below $0.5\sigma(I)$, I was set to $0.25\sigma(I)$. The initial structural models were determined by direct methods. The H-atoms were located in difference *Fourier* maps after anisotropic refinement of the other atoms and were refined with individual isotropic temperature factors. In **13**, one H-atom was kept fixed at the position were it was located because it could not be meaningfully refined. In the last blocked cascade refinements with *ca.* 100 variables per block, all unique reflections were used to bring the variables to convergence, **13** an exception being where only the 1784 reflections with $I > 1.5\sigma(I)$ were included. Version 2.5 of the program system SHELXTL [10] was applied for **9, 11, 13, 15**, and **21**, version 3.0 for **2, 4, 7, 19**, and **24**.

Fractional atomic coordinates (except H-atoms) are given in the *Tables 4–13* and a stereoview (arbitrary radii for the H-atoms, 50% probability ellipsoids for the others) as well as bond lengths, bond angles, and intra-annular torsion angles are presented in *Figures 5–25*.

Crystallographic Data

4	11′	15′	24′	21′	7
Et$_2$O/pentane	EtOAc/Et$_2$O/pentane	EtOAc/hexane	EtOAc/hexane	EtOAc/Et$_2$O/hexane	Et$_2$O/hexane
C$_{10}$H$_{15}$NO$_5$	C$_{11}$H$_{17}$NO$_4$	C$_{12}$H$_{19}$NO$_4$	C$_{19}$H$_{23}$NO$_6$	C$_{14}$H$_{21}$NO$_6$	C$_{13}$H$_{21}$NO$_5$
229.23	227.26	241.29	361.39	299.34	271.3
130	130	130	295	130	130
$P2_1/c$	$P2_1/c$	$C2/c$	$P2_1/c$	$P2_1/a$	$P2_1/c$
4	4	8	4	4	4
15.505(3)	13.187(3)	31.904(18)	11.863(1)	10.984(2)	9.758(1)
7.442(1)	7.697(1)	5.065(2)	15.216(1)	12.647(2)	13.707(2)
10.032(1)	10.892(2)	15.321(7)	10.402(1)	11.395(1)	10.814(1)
105.41(1)	95.12(1)	102.66(3)	107.05(1)	112.30(1)	105.40(1)
80	29	51	120	25	72
$40 < |2\Theta| < 51$	$39 < |2\Theta| < 47$	$31 < |2\Theta| < 40$	$35 < |2\Theta| < 49$	$36 < 2\Theta < 44$	$42 < |2\Theta| < 51$
1.33	1.37	1.33	1.34	1.36	1.29
63	70	60	58	50	70
3700	4861	3490	4766	2562	6137
205	213	230	327	274	256
0.084	0.068	0.087	0.116	0.044	0.133
0.082	0.065	0.067	0.097	0.049	0.128
$\sigma_F^2 + 0.0002F^2$	$\sigma_F^2 + 0.0007F^2$	$\sigma_F^2 + 0.0006F^2$	$\dfrac{\sigma_F^2 + 0.0004\,F^2}{1-e^{-20s^2}}$	$\sigma_F^2 + 0.0004F^2$	$\sigma_F^2 + 0.002F^2$

[b]) $s = \sin\Theta/\lambda$.

The data sets of **13** and **24** could not be obtained at low temperature because the crystals fractured upon cooling, probably due to phase transitions, a phenomenon observed also with other medium-sized rings [11].

In the following discussion, *Dale*'s nomenclature [12] is used for rings with more than 8 members to describe their conformation. According to this nomenclature, the numbers of bonds between corner atoms are indicated between square brackets, *e.g.* [2323] for a cyclodecane ring (note that lit. ref. have at most 2 digits). A 'corner atom' is defined as an atom located on the apices of 2 gauche torsion angles of equal sign. Two atoms connected by a (Z)-configurated double bond are always considered as corner atoms, and the double bond is indicated by an italic *1* [13], *e.g.* [*1*233] for a cyclononane. This is only a rough, by no means unique, classification which, in many cases, provides a reasonable estimate of the general shape of the ring.

Bonds, bond angles, and torsion angles are designated by concatenating the symbols of the atoms involved. A capital letter outside parentheses indicates the beginning of a new atom symbol. A bond is represented by 2 atom symbols, an angle by 3, and a torsion angle by 4. The term 'transannular' is used to indicate *e.g.* the intra-annular distance between 2 H-atoms which are separated by at least 5 bonds (2 CH and *e.g.* 3 CC bonds). Transannular HH distances given in this paper are calculated from 'idealized' H positions (CH 1.08 Å, HCH 109.5°) rather than from the observed values because of the poor accuracy in their location by X-ray diffraction methods. This assumption includes the risk that real CCH or HCH angle distortions will remain undetermined.

Of the 10 structures described here, 7 have 1,3-diketone or tricarbonylmethane moieties. In 5 of the latter 7 structures, one keto group is enolized. In the following, a prime is added to their numbers to distinguish them from their all-keto structures in *Schemes 1* and *2*. In all the enolized structures, the 1,3-diketone moieties have 'cis'-conformations with a H-bond between the two O-atoms. As expected, the ester groups retain their carbonyl function in **21′** and **24′**, and another keto group is enolized. The *Figs. 1, 2, 3*, and *4* show difference *Fourier* plots (contour interval 0.1 e$^-$/Å^3, negative contours dashed, without zero contour) in which the enolic H-atom was omitted from the calculated structure factors. In *Fig. 1*, two electron-density maxima appear near the *position of this*
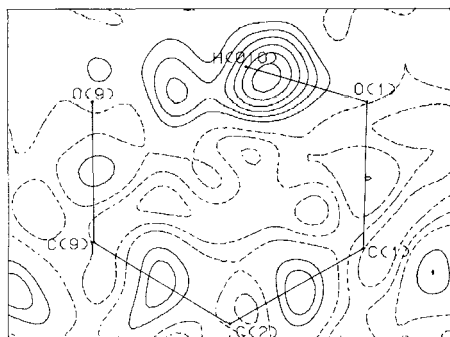
Fig. 1. *Difference Fourier plot in the plane of the enolized 1,3-diketone system of* **9′**
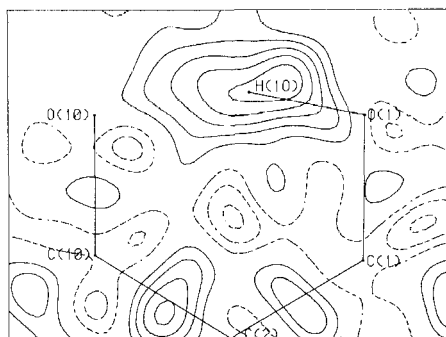

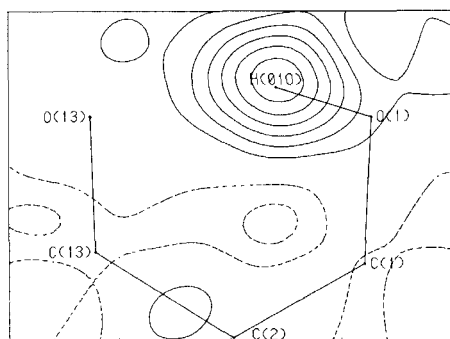Fig. 2. *Difference Fourier plot in the plane of the enolized 1,3-diketone system of* **11′**

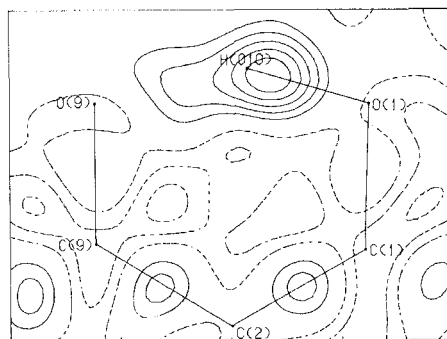Fig. 3. *Difference Fourier plot in the plane of the enolized 1,3-diketone system of* **21′**

Fig. 4. *Difference Fourier plot in the plane of the enolized 1,3-diketone system of* **9′** *at lower resolution*

H-atom of structure **9′**, the higher being 0.94 Å from O(1), the lower 0.77 Å from O(9). We, therefore, assume that the alternate enolization may also take place. (It should be remembered, however, that the X-ray experiment cannot determine, if there is also nuclear density near the lower maximum, or if it results from polarisation of the electron density at O(9) or at the enolized H-atom.) The difference density plots of **11′** and the ester **21′** do not show a second maximum for their respective H-atoms. This may indicate that the alternate enolization takes place only to a small extent, or it can be explained by the lower resolution of these data sets, especially in the case of **21′**, for which d_{min} is 0.84 Å as compared to 0.62 Å in **11′** and 0.59 Å in **9′**. When a difference electron density plot for **9′** is calculated at 0.71 Å resolution, the second maximum appears only as a shoulder of the

Table 2. *Distances* (in Å) *and the OHO Angle* (in degrees) *in the Enolized 1,3-Diketo Systems*

	1	2	3	4	5	6	7	OHO
9′	1.323(1)	1.268(1)	1.386(1)	1.440(1)	2.476(1)	1.14(3)	1.42(3)	150(3)
21′	1.332(2)	1.228(2)	1.368(2)	1.465(2)	2.533(2)	0.90(2)	1.70(2)	152(2)
11′	1.319(1)	1.270(1)	1.393(1)	1.438(1)	2.438(1)	1.06(2)	1.41(2)	161(2)
15′	1.317(2)	1.272(2)	1.392(2)	1.435(2)	2.429(2)	1.04(3)	1.47(3)	150(3)
24′	1.320(3)	1.219(3)	1.378(3)	1.459(4)	2.547(3)	0.77(4)	1.87(4)	145(4)

Table 3. *Bond Distances* (in Å), *Bond Angles* (in degrees) *and Equivalent Isotropic Temperature Factors* (defined as one third of the trace of the orthogonalized *U* tensor, in $Å^2 \times 10^3$) *of the NO$_2$ Group*

	CN	NO	CNO	ONO	$U_{eq}(N)$	$U_{eq}(O)$
19	1.542(1)	1.224(1)	120.5(1)	122.8(1)	201(2)	303(3)
		1.225(1)	116.7(1)			331(3)
2	1.539(1)	1.224(1)	118.8(1)	122.6(1)	180(2)	286(3)
		1.226(1)	118.5(1)			291(3)
13	1.547(5)	1.175(6)	119.8(5)	123.3(4)	740(20)	1034(19)
		1.244(7)	116.9(3)			1215(22)
9′	1.522(1)	1.225(1)	119.3(1)	123.7(1)	168(2)	265(2)
		1.230(1)	116.9(1)			236(2)
4	1.516(3)	1.176(2)	121.0(2)	120.2(2)	342(4)	705(6)
		1.156(4)	118.8(2)			1767(8)
11′	1.514(1)	1.229(1)	117.7(1)	123.7(1)	175(4)	270(2)
		1.227(1)	118.6(1)			241(2)
15′	1.521(2)	1.219(2)	119.6(1)	123.2(2)	250(4)	428(5)
		1.222(2)	117.2(1)			378(4)
24′	1.516(4)	1.205(4)	115.9(3)	123.4(3)	481(9)	612(9)
		1.204(3)	120.7(2)			1165(18)
21′	1.529(2)	1.222(2)	117.9(1)	123.9(1)	281(4)	391(4)
		1.224(2)	118.1(1)			403(4)
7	1.514(2)	1.183(3)	117.7(2)	123.3(2)	491(6)	838(9)
		1.201(3)	118.9(2)			1276(14)

stronger peak (see *Fig. 4*). Bond lengths of the enolized 1,3-diketo systems are given in *Table 2*. They show that the carbonyl groups in the esters **21′** and **24′** retain a short distance, while it is significantly elongated in the other 3 compounds. Other bonds show related effects but with lesser significance.

Since each compound described here contains a NO$_2$ group, it seemed appropriate to consider its geometry. Bond lengths and angles are given in *Table 3*. The NO distances range from 1.156 to 1.244 Å. However, in case of restriction only to structures with sufficiently small thermal parameters, the 12 selected values only range from 1.219 to 1.230 Å with an unweighted mean of 1.225 Å. The N-atoms are bound to tertiary C-atoms at distances between 1.514 and 1.529 Å, mean 1.519 Å (7 values), and to
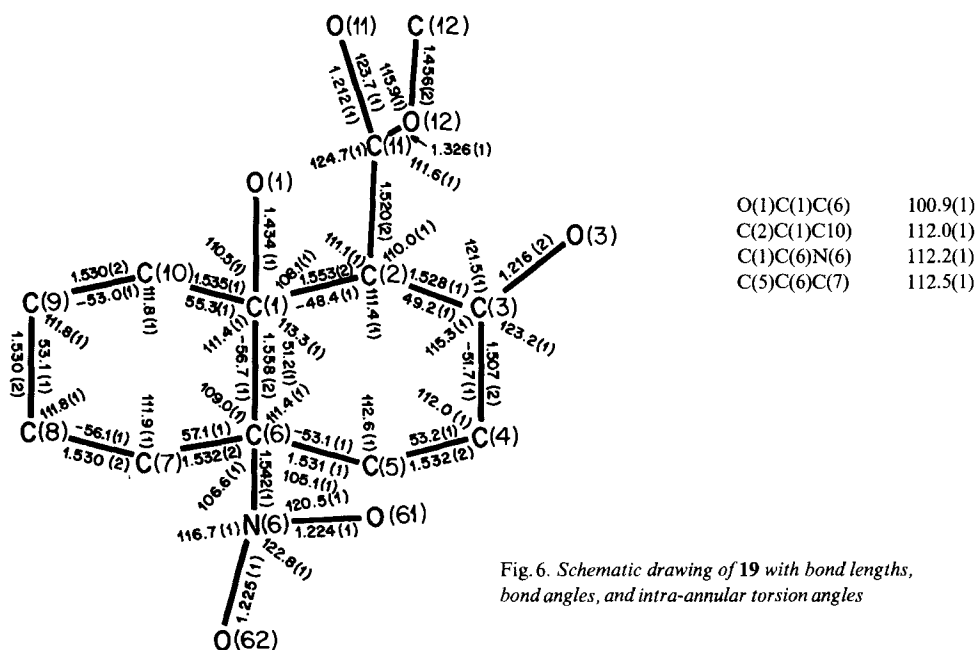

Fig. 5. Stereoview of **19**

O(1)C(1)C(6)	100.9(1)
C(2)C(1)C10)	112.0(1)
C(1)C(6)N(6)	112.2(1)
C(5)C(6)C(7)	112.5(1)
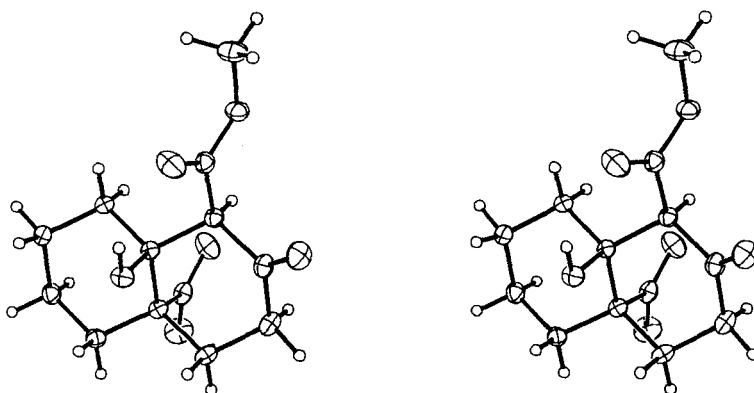
Fig. 6. *Schematic drawing of* **19** *with bond lengths, bond angles, and intra-annular torsion angles*

Table 4. *Fractional Atomic Coordinates (× 10^4) and Isotropic Temperature Factors ($\mathring{A}^2$ × 10^3) of* **19**

Atom	x	y	z	U_{eq}[a])
C(1)	2150(1)	6561(2)	3829(1)	15(1)
O(1)	2193(1)	8154(1)	3165(1)	20(1)
C(2)	3202(1)	5400(2)	4055(1)	17(1)
C(3)	4087(1)	6863(2)	4492(1)	19(1)
O(3)	4882(1)	6920(1)	4226(1)	28(1)
C(4)	3909(1)	8163(2)	5283(1)	22(1)
C(5)	2880(1)	9338(2)	5031(1)	20(1)
C(6)	1963(1)	7897(2)	4648(1)	16(1)
N(6)	1851(1)	6540(2)	5472(1)	20(1)
O(61)	2147(1)	4727(1)	5535(1)	30(1)
O(62)	1486(1)	7389(2)	6060(1)	33(1)
C(7)	946(1)	9095(2)	4330(1)	20(1)
C(8)	34(1)	7632(2)	3967(1)	22(1)
C(9)	215(1)	6248(2)	3184(1)	20(1)
C(10)	1243(1)	5077(2)	3460(1)	19(1)
C(11)	3417(1)	4391(2)	3197(1)	20(1)
O(11)	3288(1)	5232(2)	2451(1)	32(1)
O(12)	3766(1)	2458(1)	3363(1)	22(1)
C(12)	3991(1)	1345(2)	2581(1)	30(1)

[a]) Equivalent isotropic U defined as one third of the trace of the orthogonalised U tensor.

quaternary C-atoms at distances between 1.539 and 1.547 Å (3 values). Here, no selection on thermal parameters was necessary. The ONO angles show a remarkable consistency between 122.6 and 123.9° except one outlier of 120.2°. The values for the NO_2 groups bound to quaternary C-atoms are at the lower end. The CNO angles have a wider range extending from 115.9 to 121.0°.

Bicyclic **19** (see *Figs. 5* and *6*) has the conformation expected for a *trans*-decalin system. The 1,3-diketone system consisting of the ester group at C(2) and the carbonyl group C(3)O(3) is not enolized, possibly to avoid steric interactions between O(12) and C(10) and its equatorial H-atom. Instead, O(11) is involved in an H-bond with the OH group at C(1).

Compound **2** (see *Figs. 7* and *8*) is a cyclic hemiacetal having a *cis*-decalin system. From the two all-chair conformations possible for such a system, the molecule adopts the expected form, in which the CH_3 group at C(3) is equatorial. This is also the form in which only one CH_2 group is axial with respect to the other ring. The OH group at C(1) forms a H-bond to O(2) of another molecule.

The bicyclic compound **13** (see *Figs. 9* and *10*) consists of a six- and a seven-membered ring *cis* to each other. Though the two bridgehead atoms are both quaternary, the intra-annular torsion angles around their common bond are rather small. The six-membered ring may be approximately described as a slightly twisted boat. The seven-membered ring is somewhere between a chair conformation with C(1)C(7) being the eclipsed bond and a twist-chair with C(1) lying on an approximate C_2-axis (*cf.* [12] [14]). All transannular HH distances are greater than 2.1 Å.

The eight-membered ring of **9'** (*cf. Figs. 11* and *12*) contains two neighbouring trigonal C-atoms with a torsion angle near 0°. The same situation is found in the structure of enantholactam hydrochloride (7-heptanelactam hydrochloride) [15] and, indeed, the two rings are strikingly similar. The largest differences between corresponding torsion angles in the two structures, 7.2 and 4.1°, are found at the C-atom which carries the additional NO_2 group in **9'**.

In the other eight-membered ring **4**, as compared to **9'**, the Ac group is replaced by a methoxycarbonyl group, and the NO_2 group is bound to another ring atom (see *Figs. 13* and *14*). However, the 1,3-diketone system is not enolized as in **9'**, which may result from a reduced tendency of the ester group to participate in enolized 1,3-diketones and/or perhaps for conformational reasons. The NO_2 group would be bound to one of the C-atoms on the apex of the 100° torsion angle in the alternative structure. In the structure found here, the ring takes on the boat-chair conformation which is known to be the most stable conformation for cyclooctanes [16]. As expected in medium-sized rings, the trigonal C-atom has the position where otherwise transannular HH interactions would arise. The remaining transannular HH distances are $\geqslant 2.07$ Å.

For cyclononane-ring systems, it is known from force-field calculations ([17] and ref. cited therein) that they may adopt several conformations. A remarkable example of their conformational variability is the structure of capryolactam (8-octanelactam) in which the amide group is *trans*-configurated in the free base [18], whereas it is *cis*-configurated in the hydrochloride [19]. The cyclononane derivative **11'** (see *Figs. 15* and *16*) has an enolized 1,3-diketone system and, therefore, one synplanar bond in the ring. Nevertheless, its irregular conformation differs from that of capryolactam hydrochloride. According to *Dale's* nomenclature, one may describe it as a [*1*233] conformation somewhere in between a [333] and a [234] conformation in which the torsion angles strongly differ from their expected values. Two of the torsion angles between tetrahedral C-atoms are near 120° indicating the presence of *Pitzer* strain. Four transannular HH distances are between 1.94 and 2.04 Å.
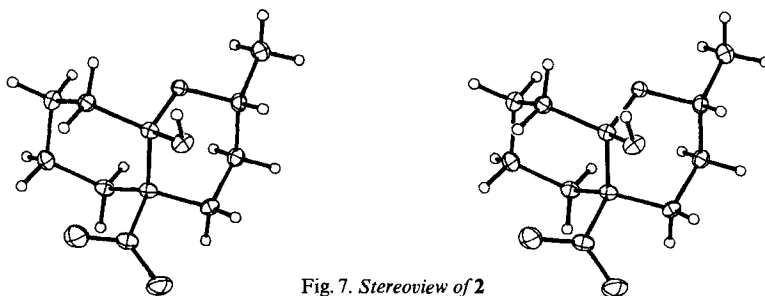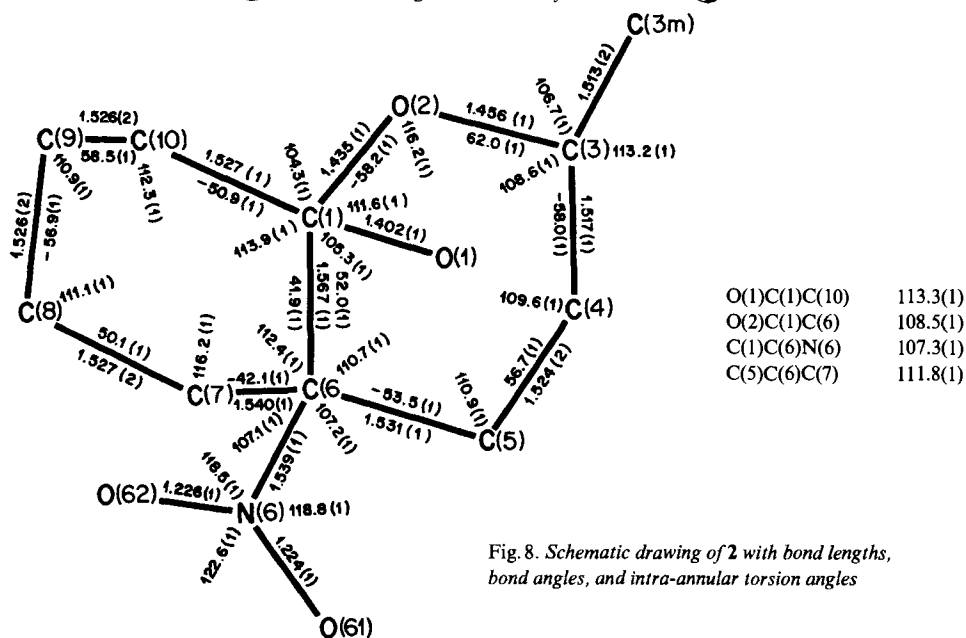
Fig. 7. *Stereoview of* **2**

O(1)C(1)C(10)	113.3(1)
O(2)C(1)C(6)	108.5(1)
C(1)C(6)N(6)	107.3(1)
C(5)C(6)C(7)	111.8(1)

Fig. 8. *Schematic drawing of* **2** *with bond lengths, bond angles, and intra-annular torsion angles*

Table 5. *Fractional Atomic Coordinates* ($\times 10^4$) *and Isotropic Temperature Factors* ($\text{Å}^2 \times 10^3$) *of* **2**

Atom	x	y	z	U_{eq}[a])
C(1)	2479(2)	3747(1)	1671(1)	14(1)
O(1)	4218(1)	4192(1)	1899(1)	18(1)
O(2)	639(1)	4238(1)	1795(1)	15(1)
C(3)	558(2)	5131(1)	1534(1)	16(1)
C(3m)	−1424(2)	5540(1)	1766(1)	24(1)
C(4)	693(2)	5073(1)	811(1)	17(1)
C(5)	2665(2)	4600(1)	622(1)	16(1)
C(6)	2782(2)	3681(1)	930(1)	14(1)
N(6)	4958(1)	3324(1)	811(1)	18(1)
O(61)	6135(1)	3758(1)	480(1)	29(1)
O(62)	5414(1)	2598(1)	1032(1)	29(1)
C(7)	1276(2)	3027(1)	616(1)	17(1)
C(8)	923(2)	2156(1)	972(1)	20(1)
C(9)	420(2)	2322(1)	1674(1)	19(1)
C(10)	2119(2)	2855(1)	1996(1)	16(1)

[a]) See *Footnote a* in *Table 4*.

Fig. 9. *Stereoview of* **13**

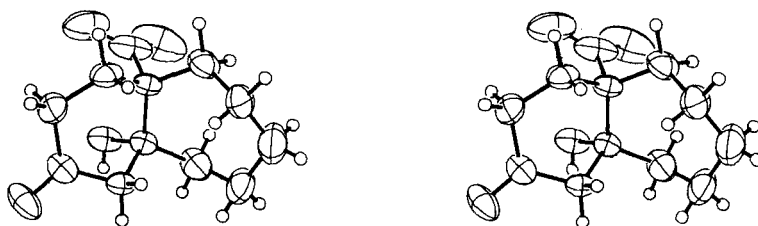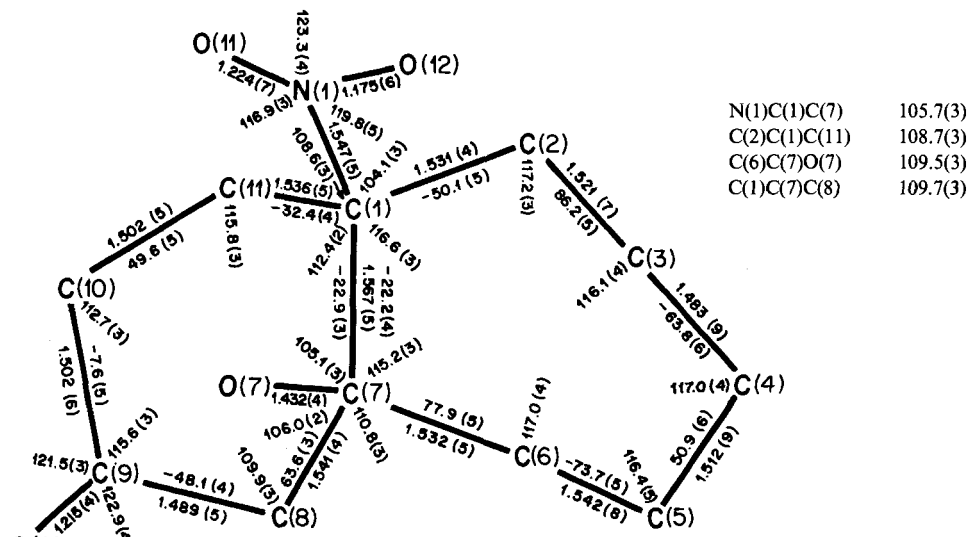|	
N(1)C(1)C(7)	105.7(3)
C(2)C(1)C(11)	108.7(3)
C(6)C(7)O(7)	109.5(3)
C(1)C(7)C(8)	109.7(3)

Fig. 10. *Schematic drawing of* **13** *with bond lengths, bond angles, and intra-annular torsion angles*

Table 6. *Fractional Atomic Coordinates (× 10⁴) and Isotropic Temperature Factors (Å² × 10³) of* **13**

Atom	x	y	z	U_{eq}[a])
C(1)	4009(4)	4109(3)	1633(3)	39(1)
N(1)	4182(7)	5281(3)	1094(3)	74(2)
O(11)	5622(5)	5627(3)	1297(3)	103(2)
O(12)	2983(6)	5811(3)	548(3)	122(2)
C(2)	2804(5)	3413(3)	616(3)	61(2)
C(3)	2054(6)	2323(4)	897(4)	68(2)
C(4)	520(7)	2487(6)	1125(5)	97(3)
C(5)	673(6)	3205(5)	2167(4)	91(3)
C(6)	1511(5)	4401(4)	2272(4)	68(2)
C(7)	3402(4)	4414(3)	2620(3)	39(1)
O(7)	4028(3)	5555(2)	2988(2)	54(1)
C(8)	4268(4)	3615(3)	3662(3)	40(1)
C(9)	6097(4)	3826(3)	4139(3)	48(1)
O(9)	6902(3)	4000(3)	5156(2)	73(1)
C(10)	6889(5)	3852(4)	3271(3)	61(2)
C(11)	5710(4)	3500(3)	2087(3)	54(2)

[a]) See *Footnote a* in *Table 4*.
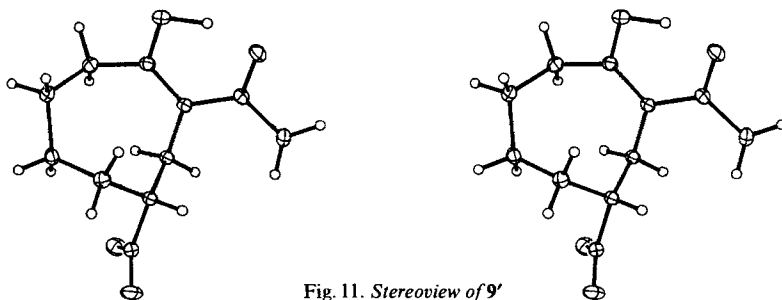
Fig. 11. *Stereoview of* **9′**

Table 7. *Fractional Atomic Coordinates* (× 10^4) *and Isotropic Temperature Factors* ($\mathring{A}^2$ × 10^3) *of* **9′**

| Atom	x	y	z	U_{eq}[a])
C(1)	3373(1)	4572(1)	1739(1)	15(1)
O(1)	3493(1)	6002(1)	1712(1)	20(1)
C(2)	2026(1)	3894(1)	1587(1)	13(1)
C(3)	1925(1)	2258(1)	1521(1)	13(1)
C(4)	1858(1)	1759(1)	289(1)	14(1)
N(4)	1776(1)	111(1)	218(1)	17(1)
O(41)	1282(1)	–416(1)	–706(1)	27(1)
O(42)	2226(1)	–614(1)	1056(1)	24(1)
C(5)	3154(1)	2216(1)	–311(1)	16(1)
C(6)	4676(1)	1900(1)	332(1)	16(1)
C(7)	5454(1)	3186(1)	964(1)	17(1)
C(8)	4804(1)	3791(1)	1991(1)	17(1)
C(9)	734(1)	4776(1)	1493(1)	15(1)
O(9)	803(1)	6150(1)	1452(1)	20(1)
C(10)	–735(1)	4094(1)	1472(1)	20(1)

[a])   See *Footnote a* in *Table 4*.
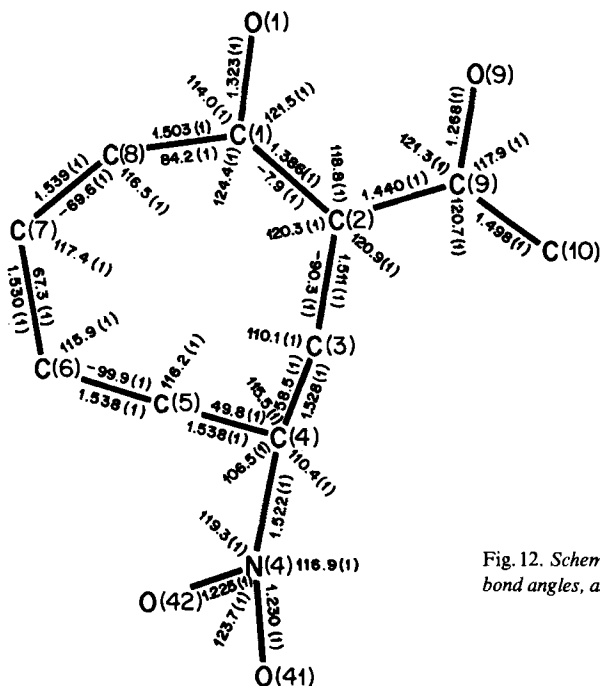
Fig. 12. *Schematic drawing of* **9′** *with bond lengths, bond angles, and intra-annular torsion angles*
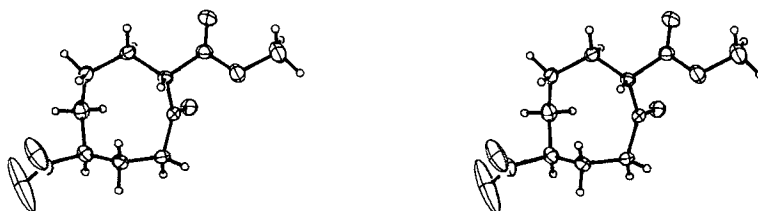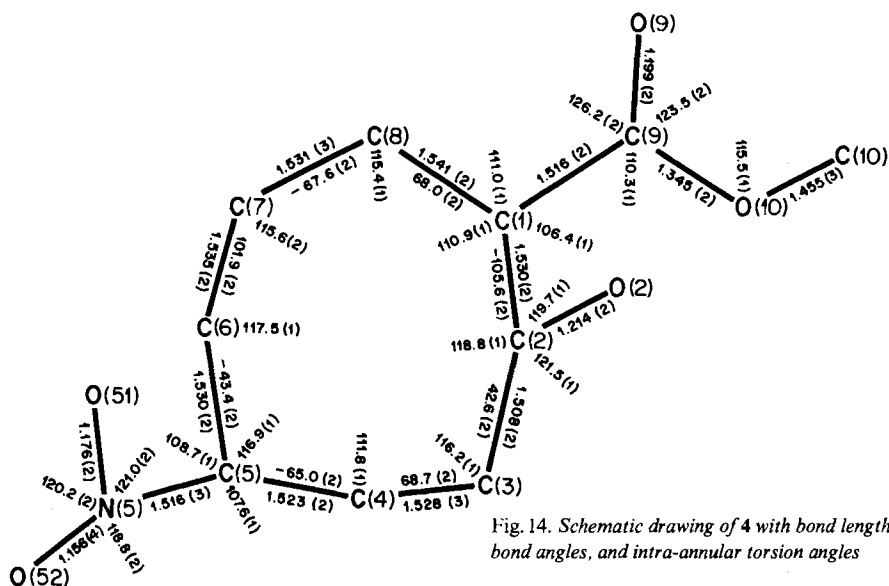
Fig. 13. *Stereoview of* 4

Fig. 14. *Schematic drawing of* 4 *with bond lengths, bond angles, and intra-annular torsion angles*

Table 8. *Fractional Atomic Coordinates* (× 10⁴) *and Isotropic Temperature Factors* (Å² × 10³) *of* 4

Atom	x	y	z	U_{eq}[a])
C(1)	1968(1)	7144(2)	1317(2)	22(1)
C(2)	2040(1)	5430(2)	2181(2)	22(1)
O(2)	2064(1)	5532(2)	3398(1)	30(1)
C(3)	2050(1)	3639(2)	1481(2)	28(1)
C(4)	2623(1)	3525(2)	457(2)	27(1)
C(5)	3617(1)	3642(2)	1182(2)	27(1)
N(5)	4125(1)	3264(2)	113(2)	34(1)
O(51)	3927(1)	3976(3)	−972(2)	71(1)
O(52)	4712(2)	2253(5)	380(3)	177(1)
C(6)	3956(1)	5412(3)	1911(2)	30(1)
C(7)	3610(1)	7163(2)	1145(2)	29(1)
C(8)	2874(1)	8130(2)	1625(2)	26(1)
C(9)	1263(1)	8301(2)	1693(2)	26(1)
O(9)	1390(1)	9701(2)	2305(2)	45(1)
O(10)	457(1)	7505(2)	1283(1)	37(1)
C(10)	−268(1)	8436(3)	1664(2)	47(1)

[a]) See *Footnote a* in *Table 4*.
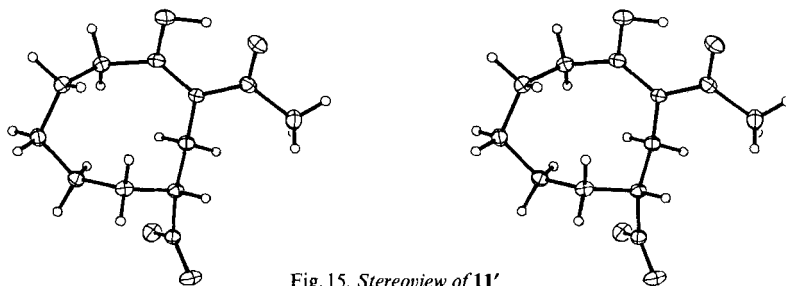
Fig. 15. *Stereoview of* **11′**

Table 9. *Fractional Atomic Coordinates* (× 10⁴) *and Isotropic Temperature Factors* (Å² × 10³) *of* **11′**

Atom	x	y	z	U_{eq}ᵃ)
C(1)	3198(1)	16497(1)	5423(1)	18(1)
O(1)	3413(1)	16979(1)	6580(1)	25(1)
C(2)	3512(1)	14889(1)	5006(1)	16(1)
C(3)	3242(1)	14283(1)	3695(1)	17(1)
C(4)	2268(1)	13172(1)	3604(1)	16(1)
N(4)	2077(1)	12408(1)	2323(1)	18(1)
O(41)	1742(1)	10921(1)	2233(1)	27(1)
O(42)	2234(1)	13322(1)	1433(1)	24(1)
C(5)	1292(1)	14131(1)	3876(1)	17(1)
C(6)	1038(1)	15744(1)	3073(1)	18(1)
C(7)	725(1)	17340(1)	3790(1)	20(1)
C(8)	1451(1)	17836(1)	4915(1)	22(1)
C(9)	2598(1)	17853(1)	4677(1)	21(1)
C(10)	4088(1)	13779(1)	5872(1)	19(1)
O(10)	4282(1)	14215(1)	6993(1)	26(1)
C(11)	4488(1)	12042(2)	5507(1)	25(1)

ᵃ) See *Footnote a* in *Table 4*.
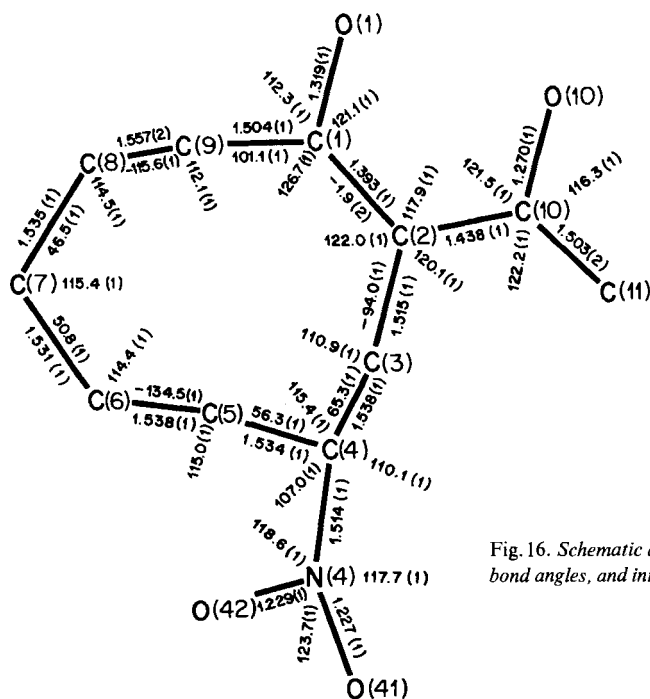
Fig. 16. *Schematic drawing of* **11′** *with bond lengths, bond angles, and intra-annular torsion angles*

The ten-membered ring **15'** (see *Figs. 17* and *18*) again has a (Z)-configurated double bond due to an enolized 1,3-diketone system. Its conformation is very similar to that of the *cis*-cyclodecene · AgNO$_3$ complex [20] and may be described as [*1*2232] conformation. It can easily be derived from the most stable form of cyclodecane (see *Fig. 19*) as established by the crystal-structure analyses of the parent [21] and some derivatives by closing the *gauche* angle between a corner atom and its adjacent ring atom on the longer side. Some of the four transannular HH distances are short (1.85, 1.87, 1.94, and 2.19 Å), and some CCC angles are widened, but there is scarcely *Pitzer* strain. Though two of the four transannular HH distances could be relieved in an enolized diketone having a '*trans*'-conformation but lacking the intramolecular H-bond, the '*cis*'-form is retained.

As mentioned before, the enolized 1,3-diketone subunit of the tricarbonylmethane system introduces a double bond into the eleven-membered ring of **24'** (see *Figs. 20* and *21*), which may be called a [*1*334] conformation. The torsion angles about the bonds from
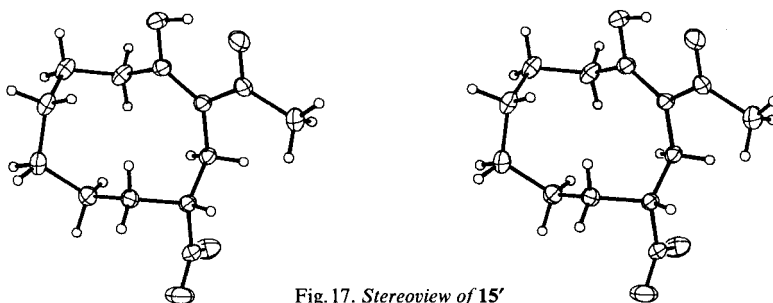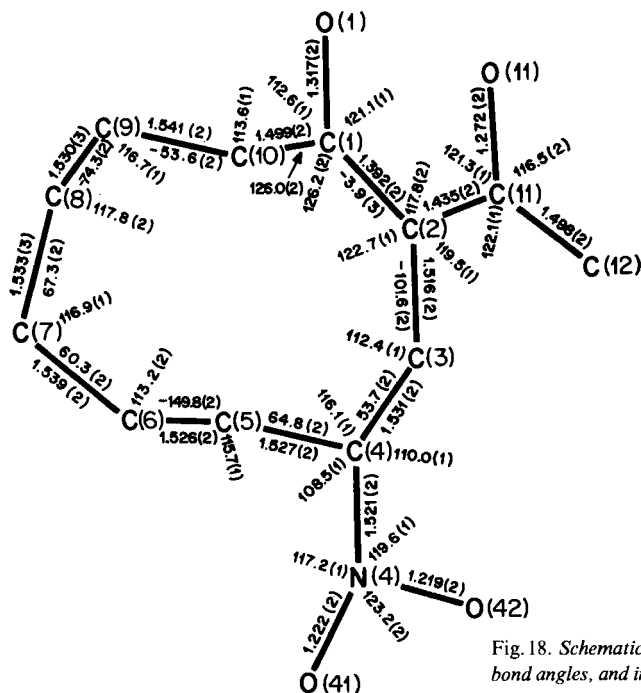

Fig. 17. *Stereoview of* **15'**

Fig. 18. *Schematic drawing of* **15'** *with bond lengths, bond angles, and intra-annular torsion angles*
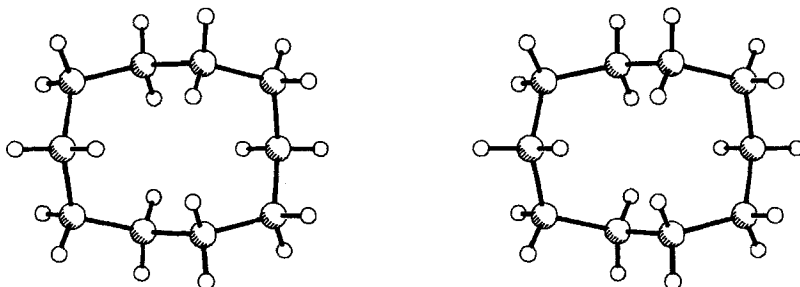
Fig. 19. *Stereoview of cyclodecane*

Table 10. *Fractional Atomic Coordinates (× 10^4) and Isotropic Temperature Factors (Å^2 × 10^3) of* **15′**

Atom	x	y	z	U_{eq}[a])
C(1)	1574(1)	4056(3)	−636(1)	23(1)
O(1)	1836(1)	2728(3)	−1029(1)	31(1)
C(2)	1138(1)	3463(3)	−800(1)	21(1)
C(3)	827(1)	4901(3)	−345(1)	21(1)
C(4)	718(1)	3306(3)	424(1)	19(1)
N(4)	423(1)	4898(3)	881(1)	25(1)
O(41)	288(1)	3804(3)	1474(1)	43(1)
O(42)	326(1)	7147(3)	635(1)	38(1)
C(5)	1100(1)	2339(3)	1137(1)	22(1)
C(6)	1373(1)	4491(4)	1683(1)	28(1)
C(7)	1848(1)	3699(5)	2004(1)	36(1)
C(8)	2096(1)	3038(4)	1281(1)	29(1)
C(9)	2181(1)	5281(4)	675(1)	30(1)
C(10)	1796(1)	6233(3)	−49(1)	28(1)
C(11)	978(1)	1456(4)	−1450(1)	25(1)
O(11)	1232(1)	102(3)	−1807(1)	34(1)
C(12)	508(1)	937(5)	−1776(1)	33(1)

[a])   See *Footnote a* in *Table 4.*

Fig. 20. *Stereoview of* **24′**

Fig. 21. *Schematic drawing of* **24′** *with bond lengths, bond angles, and intra-annular torsion angles*

Table 11. *Fractional Atomic Coordinates ($\times 10^4$) and Isotropic Temperature Factors ($\text{Å}^2 \times 10^3$) of* **24′**

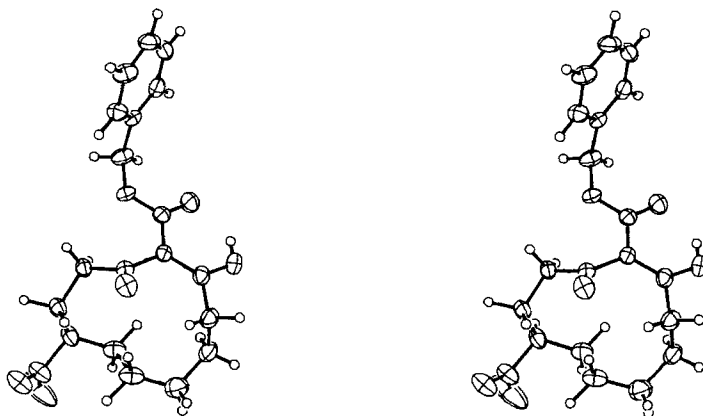| Atom	x	y	z	U_{eq}[a])
C(1)	1313(2)	1619(2)	2207(2)	26(1)
C(2)	115(2)	1725(2)	1958(3)	33(1)
O(2)	−659(2)	1241(2)	1069(2)	47(1)
C(3)	−482(2)	2428(2)	2526(3)	40(1)
C(4)	−983(2)	3152(2)	1461(3)	45(1)
C(5)	−538(3)	4076(2)	1931(3)	53(1)
C(6)	743(3)	4225(2)	2378(3)	47(1)
C(7)	1347(3)	3989(2)	1298(3)	41(1)
C(8)	2677(3)	4105(2)	1748(3)	40(1)
N(8)	3030(2)	5062(2)	1998(3)	48(1)
O(81)	3502(2)	5324(1)	3119(3)	61(1)
O(82)	2796(4)	5528(2)	1019(3)	117(2)
C(9)	3384(2)	3567(2)	2942(3)	35(1)
C(10)	3179(2)	2587(2)	2657(2)	31(1)
C(11)	2169(2)	2222(2)	3125(2)	27(1)
O(11)	2060(2)	2441(1)	4208(2)	40(1)
C(12)	1726(2)	922(2)	1493(2)	30(1)
O(12)	1087(2)	455(1)	630(2)	42(1)
O(13)	2901(2)	821(1)	1909(2)	33(1)
C(13)	3386(3)	144(2)	1233(3)	39(1)
C(14)	3595(2)	−695(2)	2015(2)	28(1)
C(15)	4133(3)	−691(2)	3404(3)	37(1)
C(16)	4387(3)	−1476(2)	4097(3)	46(1)
C(17)	4122(3)	−2266(2)	3426(4)	46(1)
C(18)	3573(3)	−2275(2)	2069(4)	46(1)
C(19)	3303(2)	−1499(2)	1364(3)	36(1)

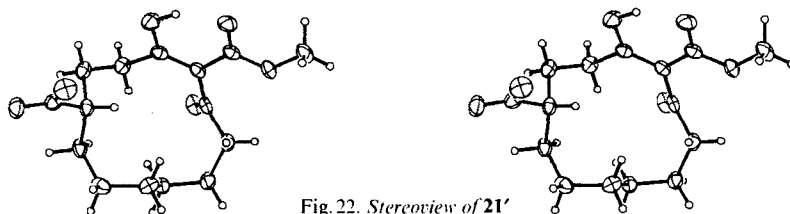[a]) See *Footnote a* in *Table 4*.
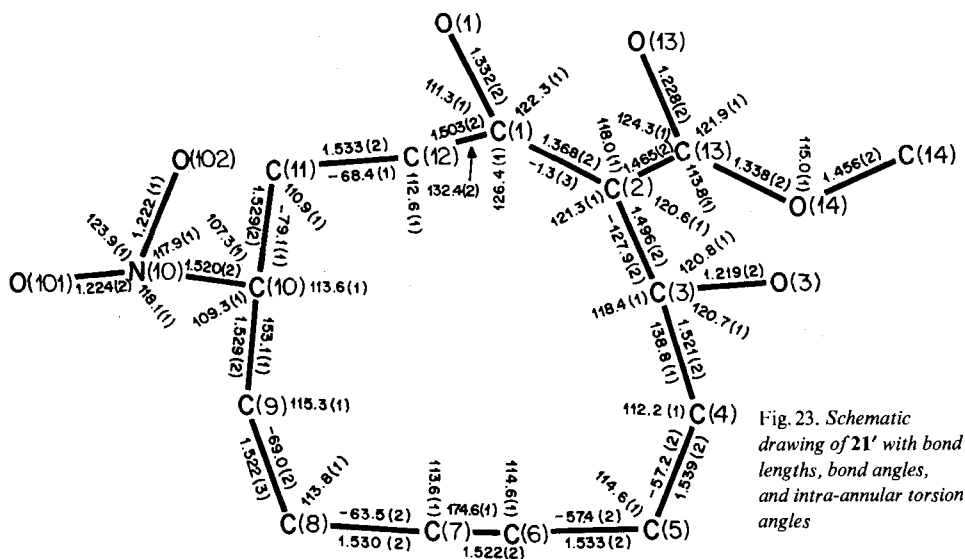
Fig. 22. *Stereoview of* **21′**

Fig. 23. *Schematic drawing of* **21′** *with bond lengths, bond angles, and intra-annular torsion angles*

Table 12. *Fractional Atomic Coordinates* ($\times 10^4$) *and Isotropic Temperature Factors* ($\text{Å}^2 \times 10^3$) *of* **21′**

Atom	x	y	z	U_{eq} [a]
C(1)	3751(1)	3955(1)	2201(1)	26(1)
O(1)	2772(1)	3972(1)	1064(1)	37(1)
C(2)	4599(1)	3118(1)	2608(1)	24(1)
C(3)	5738(2)	3143(1)	3858(1)	25(1)
O(3)	5582(1)	3409(1)	4821(1)	34(1)
C(4)	7108(2)	2888(1)	3890(1)	30(1)
C(5)	8172(2)	3626(1)	4786(2)	34(1)
C(6)	7927(1)	4807(1)	4480(1)	28(1)
C(7)	7791(2)	5113(1)	3145(1)	32(1)
C(8)	7419(2)	6273(1)	2822(2)	35(1)
C(9)	6072(2)	6568(1)	2824(1)	31(1)
C(10)	4891(1)	6084(1)	1754(1)	25(1)
N(10)	4499(1)	6796(1)	594(1)	28(1)
O(101)	4372(1)	7743(1)	739(1)	39(1)
O(102)	4273(1)	6381(1)	−436(1)	40(1)
C(11)	3673(2)	5948(1)	2087(1)	28(1)
C(12)	3803(1)	4965(1)	2912(1)	28(1)
C(13)	4386(1)	2203(1)	1764(1)	26(1)
O(13)	3523(1)	2151(1)	695(1)	35(1)
O(14)	5193(1)	1391(1)	2283(1)	30(1)
C(14)	5012(2)	472(1)	1464(2)	37(1)

[a]　See *Footnote a* in *Table 4*.

C(3) to C(9) are similar to those found in the [335] conformation of cycloundecanone and its phenylsemicarbazone [22] including a torsion angle of *ca.* 120°. The third carbonyl group of the tricarbonylmethane system is only partially conjugated to the remainder of this group as can be seen from the torsion angles C(2)C(1)C(11)O(11) and
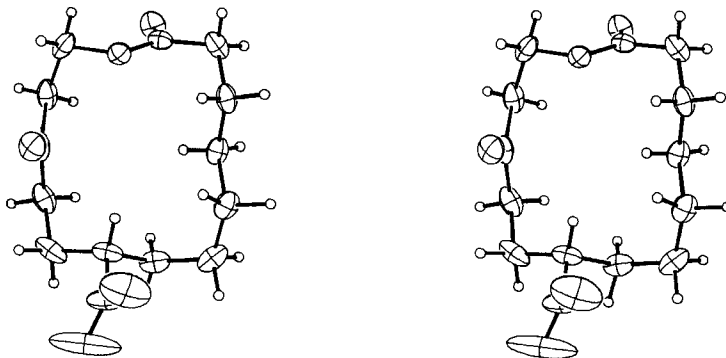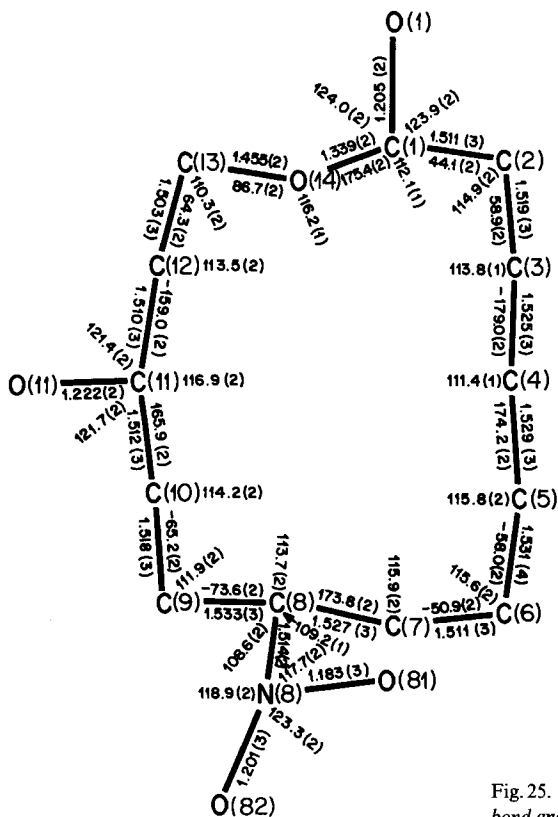

Fig. 24. *Stereoview of 7*

Fig. 25. *Schematic drawing of 7 with bond lengths, bond angles, and intra-annular torsion angles*

Table 13. *Fractional Atomic Coordinates* (× 10⁴) *and Isotropic Temperature Factors* (Å² × 10³) *of* **7**

Atom	x	y	z	U_{eq}[a])
C(1)	5798(2)	4342(1)	3385(2)	29(1)
O(1)	6572(2)	4614(1)	4389(1)	40(1)
C(2)	5380(2)	4964(2)	2191(2)	39(1)
C(3)	3818(2)	4913(2)	1465(2)	36(1)
C(4)	2811(2)	5217(2)	2259(2)	34(1)
C(5)	1257(2)	5132(2)	1486(2)	39(1)
C(6)	150(3)	5324(2)	2229(2)	46(1)
C(7)	248(2)	4675(2)	3379(2)	39(1)
C(8)	313(2)	3580(2)	3141(2)	34(1)
N(8)	–1071(2)	3257(2)	2223(2)	49(1)
O(81)	–1079(2)	3125(2)	1140(2)	84(1)
O(82)	–2076(2)	3100(3)	2636(3)	128(1)
C(9)	572(2)	2963(2)	4365(2)	46(1)
C(10)	2097(3)	3042(2)	5179(2)	41(1)
C(11)	3183(2)	2625(1)	4555(2)	33(1)
O(11)	2839(2)	2096(1)	3614(2)	42(1)
C(12)	4719(2)	2886(1)	5156(2)	39(1)
C(13)	5652(2)	2770(1)	4261(2)	38(1)
O(14)	5223(1)	3450(1)	3193(1)	30(1)

[a])   See *Footnote a* in *Table 4*.

C(12)C(1)C(11)O(11), 44.9 and –138.1°, respectively. All transannular HH distances are greater than 2 Å; the distance between O(11) and one H-atom at C(3) is 2.22 Å. With two exceptions near 118°, the CCC angles of tetrahedral C-atoms are between 110.5 and 114.3°.

Besides the alkyl moiety of the ester group, **21′** (see *Figs. 22* and *23*) differs from **24′** only by an additional CH₂ group in the ring system. In **21′**, however, it is the carbonyl function closer to the nitro group which is enolized. The degree of conjugation of the other carbonyl group with the remainder of the tricarbonylmethane system is approximately the same as in **24′**, C(1)C(2)C(3)O(3) 48.8°, C(13)C(2)C(3)O(3) –133.1°. The [12333] conformation of the twelve-membered ring can be derived from the most stable [3333] conformation of cyclododecane in a way analogous to that of **15′** from cyclodecane. No transannular HH distance is shorter than 2 Å. The shortest transannular OH distance, 2.37 Å, is between O(3)- and one H-atom of C(12). The intra-annular bond and torsion angles indicate no noteworthy *Baeyer* or *Pitzer* strain.

The fourteen-membered lactone ring of **7** (see *Figs. 24* and *25*) has a conformation analogous to that of cyclodecane and cyclododecane with 4 corner atoms and, except for the short side of cyclodecane, a 'zigzag' chain in between. It, therefore, may be described as [3434] conformation, and it is very similar to that of cyclotetradecane oxime [23]. The shortest transannular HH distance is 2.11 Å. Neither the intra-annular bond nor torsion angles indicate significant strain.

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