Phenylhydrazone Derivatives of Dimedone: Hydrogen Bonding, Spectral (^{13}C and ^1H Nuclear Magnetic Resonance) and Conformational Considerations. Crystal and Molecular Structures of 5,5-Dimethylcyclohexane-1,2,3-trione 2-(4-Methylphenylhydrazone) (1) and 5,5-Dimethylcyclohexane-1,2,3-trione 2-(4-Nitrophenylhydrazone) (2)

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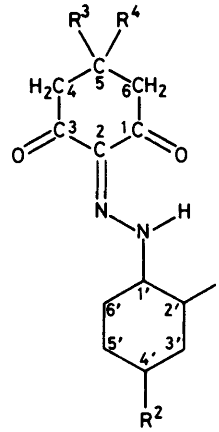
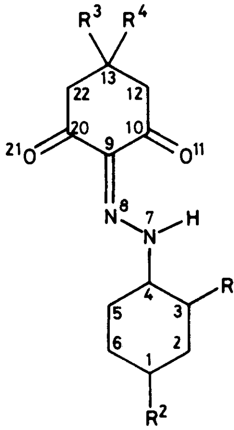
A series of phenylhydrazone derivatives of 5,5-dimethylcyclohexane-1,3-dione (dimedone) have been prepared. Their i.r. and ^1H n.m.r. spectra are discussed in terms of the extent of intramolecular hydrogen bonding. With *o*-nitro-group substituents on the aromatic ring, enhanced low-field chemical shifts of the order δ_{NH} *ca.* 15—16 imply a bifurcated hydrogen bonding environment. Compound (1), $C_{15}H_{18}N_2O_3$, is monoclinic, space group $P2_1/n$, $Z = 4$, cell dimensions $a = 14.053(8)$, $b = 5.84(1)$, $c = 16.789(7)$ Å, $\beta = 98.9(1)°$. Compound (2), $C_{14}H_{15}N_3O_5$, is triclinic, space group $P\bar{1}$, $Z = 2$, $a = 7.20(1)$, $b = 13.45(1)$, $c = 7.45(1)$ Å, $\alpha = 97.97(5)$, $\beta = 94.24(5)$, $\gamma = 98.29(5)°$. Both structures were solved by the statistical method and refined using full-matrix least-squares. The numbers of reflections used in the refinement and the final *R* values are 853, 0.087 and 1 638, 0.078 for (1) and (2) respectively. In (2), the $NO_2 \cdots HN$ and $C{=}O \cdots HN$ separations confirm the *o*-nitro-involvement in bifurcated intramolecular hydrogen bonding only. In both structures, the cyclohexane ring has an envelope conformation with the C-13 atom † 0.68 Å from the plane of the other five.

In recent papers from these laboratories we have reported structural and spectral characterisation of a variety of phenylhydrazones of mono-, di-, and tri-ketones.[1-4] Following the description of derivatives of Meldrum's acid,[5] we now turn our attention to a similar series of another cyclic 1,3-dione, *viz.* dimedone (5,5-dimethylcyclohexane-1,3-dione) and its non-methyl substituted analogue cyclohexane-1,3-dione. Nine compounds (1)—(9) are reported together with structural parameters for two of these, *i.e.* (1) and (2). Such compounds have been extensively used as precursors of potential antidiabetic drugs.[6] Polarographic $E_{\frac{1}{2}}$ studies indicate that their reduction occurs in one 4e step; the proposed mechanism involves reductive cleavage of the N–N bond as an initial step.[7]



Spectroscopic numbering

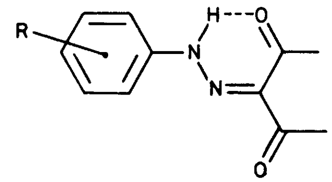


Crystallographic numbering

	R^1	R^2	R^3	R^4
(1)	H	CH_3	CH_3	CH_3
(2)	H	NO_2	CH_3	CH_3
(3)	Cl	H	CH_3	CH_3
(4)	H	H	CH_3	CH_3
(5)	H	Cl	H	H
(6)	Cl	H	H	H
(7)	H	H	H	H
(8)	NO_2	H	H	H
(9)	H	NO_2	H	H

RESULTS AND DISCUSSION

Two problems are approached and discussed for this particular series of phenylhydrazones. First, there is the question of the geometry relationships within the framework (A) as affected by substituents R and the extent of intramolecular N–H $\cdots$ O=C hydrogen bonding. Secondly, what is the preferred conformation of the dimedone ring system?



(A)

The crystallographic numbering scheme which has been used consistently in previous phenylhydrazone structures [1-5] is retained here.

^1H *N.m.r.*‡—Proton noise-decoupled spectra were obtained in $CDCl_3$ solutions at room temperature with chemical shifts measured relative to internal $SiMe_4$ (Table 1). A low-field singlet, δ_{NH} *ca.* 15, confirms strong intramolecular NH $\cdots$ O=C hydrogen bonding which, in turn, is evidently sensitive to the particular *ortho*-substituent R^1 on the aromatic ring. Trends within the series show a maximum chemical shift for *o*-nitro-group substitution. In fact δ_{NH} 15.89 is observed for (8) which is the largest downfield shift of all the compounds we have investigated to date. There is a mini-

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† Crystallographic numbering scheme.
‡ Spectroscopic numbering scheme used in this section.

mum value for compounds with a *p*-nitro-group. Methyl substituents on the aromatic ring (R^2) give one singlet, δ_{CH_3} 2.34; those associated with the dimedone ring (R^3,R^4) appear as a single signal, δ_{CH_3} 1.12—1.16, as an average from rapidly interconverting conformers. The methylene signals also reflect rapid mobility of the dione ring at room temperature. For compounds where $R^3 = R^4 = H$, the expected triplet and quintuplet in the ratio 4 : 2 are observed for C-4 and -6 (δ *ca.* 2.7) and the unique C-5 (δ *ca* 2.1) atoms, respectively. These signals broaden with loss of definition on cooling (223 K). On raising the temperature (303 K) both show unresolved multiplet fine structure (triplet > quintuplet) more conspicuously for compounds (6) and (8) which feature *o*-chloro- and *o*-nitro-groups, respectively. With $R^3 = R^4 = CH_3$ the two methylene groups at C-4 and -6 appear as a singlet (δ *ca.* 2.6) with no hint of splitting over the range 223—303 K.

TABLE 1

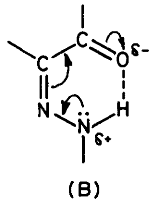
Microanalytical and ^1H n.m.r. spectral data of compounds (1)—(9) [a]

Compd.	Empirical formula	M.p. (K)	C^{calc}_{obs} (%)	H^{calc}_{obs} (%)	N^{calc}_{obs} (%)	δ_{NH}	$\delta_{CH_2}(R^1R^2)$	$\delta_{CH_3}(R^3R^4)$	δ_{CH_2}
(1)	$C_{15}H_{18}N_2O_2$	428—429	69.7/69.5	7.0/6.8	10.8/10.5	15.51	2.35 (s)	1.12 (s)	2.59 (s) [4]
(2)	$C_{14}H_{15}N_3O_4$	472—474	58.1/57.8	5.2/5.0	14.5/14.2	15.09		1.16 (s)	2.67 (s) [4]
(3)	$C_{14}H_{15}ClN_2O_2$	397—398	60.3/60.0	5.4/5.2	10.1/10.1	15.46		1.14 (s)	2.64 (s) [4]
(4)	$C_{14}H_{16}N_2O_2$	412—413	68.8/68.5	6.6/6.1	11.5/11.2	15.39		1.12 (s)	2.59 (s) [4]
(5)	$C_{12}H_{11}ClN_2O_2$	456—457	57.5/57.1	4.4/4.3	11.2/11.0	15.35			2.72 (t) [4], 2.10 (q) [2]
(6)	$C_{12}H_{11}ClN_2O_2$	399—400	57.5/57.1	4.4/4.3	11.2/11.0	15.47			2.75 (t) [4], 2.13 (q) [2]
(7)	$C_{12}H_{11}N_3O_4$	481—483	55.2/55.5	4.2/4.1	16.1/16.1	15.12			2.78 (t) [4], 2.14 (q) [2]
(8)	$C_{12}H_{11}N_3O_4$	393—394	55.2/55.1	4.2/4.1	16.1/16.0	15.89			2.79 (t) [4], 2.17 (q) [2]
(9)	$C_{13}H_{14}N_2O_2$	446—448	67.8/67.3	6.1/5.9	12.2/12.0	15.53	2.34 (s)		2.70 (t) [4], 2.05 (q) [2]

[a] δ (90 MHz) with respect to internal Me_4Si at room temperature ($CDCl_3$ solutions); (s) singlet, (t) triplet, (q) quintuplet; relative intensities [ ].

^{13}C *N.m.r.* *—Room temperature chemical shift-data for $CDCl_3$ solutions are listed in Table 2. Each compound shows the expected number of spectral lines and signal assignments are made using a combination of literature values, where appropriate, and empirical increments for benzene derivatives.[8]

Carbonyl sp^2 carbon atoms C-1 and -3 appear as separate signals in the low-field region, δ *ca.* 200 p.p.m.; these shifts are essentially unaffected by the introduction of methyl groups at C-5 in the dimethyl substituted series.[1-4] Strong intramolecular N-H · · · O=C hydrogen bonding deshields C-1 with respect to C-3 to the extent of *ca.* 5 p.p.m. Polarisation changes of the carbonyl bond through π-conjugation with restricted rotation about the N-N bond as in (B) may well be accompanying factors.



(B)

Aromatic ring carbons (δ 100—150 p.p.m.) reflect variations due to the presence of *o*- and *p*-substituents.[9] C-1′ and C-*n*′ (where *n*′ carries a substituent) and C-2 are identified by their relative low intensities due to longer relaxation times and lower nuclear Overhauser effects. The aliphatic carbons of R^2, R^3, and R^4 and the methylene groups of the dimedone ring are readily assigned by relative chemical shifts and peak heights, *e.g.* (1) shows signals for $R^2 = CH_3$ at δ 20.6 p.p.m. [26] and for $R^3 = R^4 = CH_3$ at 28.1 p.p.m. [58]. For compounds (1)—(4) retention of a single signal for $R^3 = R^4 = CH_3$ at δ 28.1—28.3 p.p.m. denies any conformational preference. C-5, the carbon furthest from the carbonyl groups, gives a single line whose position shows a characteristic upfield shift of the order of δ 20—22 p.p.m. with respect to C-4 and -6 throughout both series. With two exceptions, each of the methylene carbons C-4 and -6 gives a separate signal in both methyl-substituted [*e.g.* (2), δ 52.29 and 52.18 p.p.m.] and non-methyl-substituted compounds [*e.g.* (7), δ 39.24 and 39.03 p.p.m.]. Shielding differences for these carbons with rapidly changing axial $\rightleftharpoons$ equatorial configurations are within 0.5 p.p.m.; a reflection, perhaps, of some subtle geometry and/or electronic charge asymmetry within the dimedone ring brought about by hydrogen bonding. Coalescence into one signal for C-4 and -6 in the cases of (5) and (8) merely suggests a chemical shift difference too small to be detected under our experimental conditions.

Crystal Structures. †—The structures of (1) and (2) are shown in Figures 1 and 2, respectively. There is immediate confirmation of intramolecular hydrogen bonding between O(11) and H(7) atoms. The N(7) · · · O(11) separation is 2.63 Å in each structure. It seems clear from previous studies [1-5] that the character of the C=O · · · H-N hydrogen bonding markedly affects the geometry of (A). Where terminal groups in conjugation with C(9)-N(8) give strong hydrogen bonding, a general pattern can be recognised wherein a relative increase in the N(7)-N(8) bond length gives a corresponding de-

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* Spectroscopic numbering scheme used in this section.

† Crystallographic numbering scheme used in this section.

TABLE 2

^{13}C Chemical shifts (100.62 MHz) of compounds (1)—(9)taken in $CDCl_3$ solutions at room temperature [a]

Compd.	C-1	C-2	C-3	(C-4, C-6)	C-5	R^3,R^4	C-1′	C-2′	C-3′	C-4′	C-5′	C-6′	R^2
(1)	196.2	129.8	192.3	(52.24, 52.09)	30.2	(28.1)	138.6	117.0	129.8	136.8	129.8	117.0	20.6
(2)	196.5	130.1	192.3	(52.29, 52.18)	30.2	(28.1)	140.9	117.0	129.2	126.6	129.2	117.0	
(3)	196.6	131.3	192.6	(52.55, 52.41)	30.3	(28.2)	138.0	122.5	129.4	128.0	126.8	117.6	
(4)	197.8	131.8	192.6	(52.80, 52.68)	30.4	(28.3)	146.2	116.9	125.4	145.4	125.4	116.9	
(5)	197.5	132.2	193.0	(38.8)	18.4		139.7	118.4	129.6	131.5	129.6	118.4	
(6)	197.0	132.3	193.0	(38.73, 38.65)	18.1		137.8	122.5	129.3	126.7	127.9	117.5	
(7)	198.3	133.0	193.3	(39.24, 39.03)	18.2		146.2	117.0	125.5	145.6	125.5	117.0	
(8)	196.7	133.8	193.2	(39.1)	17.9		137.9	136.2	125.0	125.6	135.5	118.4	
(9)	196.9	131.0	193.0	(38.65, 38.58)	18.5		138.7	117.3	129.9	137.1	129.9	117.3	20.7

[a] δ (p.p.m.) with respect to internal standard $CDCl_3$ at 76.90 p.p.m

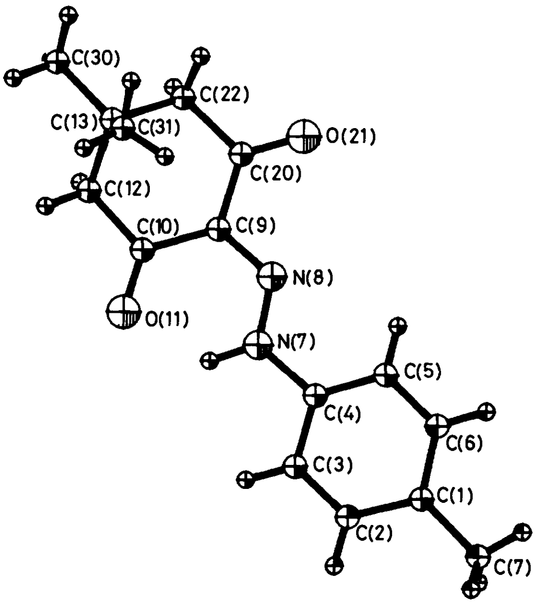


FIGURE 1

crease in the C(4)–N(7) and N(8)–C(9) bond lengths, respectively. Data for these 'pointer' dimensions of (A) obtained for (1) and (2) are in accord with the proposed interbond relationships and are listed in Table 3. For comparison, similar data obtained in previous studies are also included in Table 3 with mean distances C(4)–N(7) 1.404, N(7)–N(8) 1.314, and N(8)–C(9) 1.312 Å. Other data collected from the literature (eight such derivatives) give mean distances of 1.41, 1.34, and 1.31 Å, respectively.[3] Of course these dimensions may depend to some extent on the nature of the *ortho*- and *para*-substituents but no definite trends are discernible. The main effect of *ortho*-substitution in the aromatic ring concerns the bond angles at C(4). In general for R^1 = NO_2 there is a marked increase in the N(7)–C(4)–C(5) angle with a concomitant decrease in the N(7)–C(4)–C(3) angle by virtue of the additional $-NO_2 \cdots HN$ hydrogen bonding.[5] For other substituents, *e.g.* R^1 = Cl [5] or CH_3 [4] where no such bifurcated hydrogen bonding is feasible, the angle N(7)–C(4)–C(5) is greater than N(7)–C(4)–C(3) but by a much smaller margin. Variations in the angles in the present instance with R^1 are minimal, *e.g.* (1)(2), C(5)–C(4)–N(7) 121.4, 121.5°; N(7)–C(4)–C(3) 116.5, 118.0°. That N(8)–C(9)–C(10) is greater than N(8)–C(9)–C(20) to the extent of *ca.* 10°, *viz.* (1) 123.3, 114.7°; (2) 125.1, 114.3° is consistent with the realisation of an acceptable geometry for maximal hydrogen-bond formation [O(11) $\cdots$ H(7)]. Predictably, for *para*-substitution, variations in the 120° bond angle at C(1) are minuscule, no matter what the group.

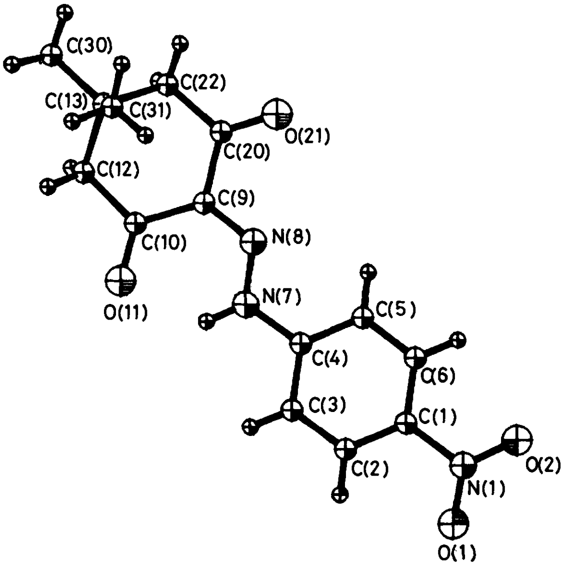


FIGURE 2

TABLE 3

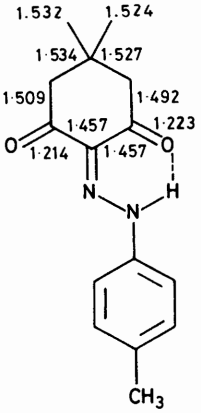
Bond lengths (Å) for the $>$C(4)–N(7)H(7)–N(8)=C(9) fragment

Compound	Reference	C(4)–N(7)	N(7)–N(8)	N(8)–C(9)
(3)	3	1.434	1.324	1.330
(4)	3	1.380	1.357	1.294
Part A	2	1.434	1.332	1.298
Part B	2	1.401	1.302	1.310
(1)	5	1.411	1.313	1.318
(2A)	5	1.374	1.295	1.305
(2B)	5	1.414	1.294	1.298
(1)	4	1.412	1.302	1.313
(2A)	4	1.375	1.325	1.292
(2B)	4	1.380	1.305	1.339
(1)	This work	1.429	1.307	1.336
(2)	This work	1.405	1.314	1.308
	Mean	1.404	1.314	1.312

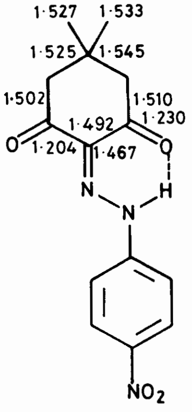
Another feature of interest centres on the deviations of atoms N(7), N(8), C(9), C(10), and C(20) from the benzene-ring plane. Consider C(10) and C(20): when these are not interconnected in the sense of being part of a six-membered ring, their deviations from the aromatic-ring plane are evidently dependent on both the presence (or otherwise) and, to a lesser extent, the particular nature of *ortho*-substituents at R^1. *E.g.* deviations rising to a maximum of 0.5 Å for the substituent of minimal steric bulk (R^1 = H) have been observed.[3]

In the present structures, these deviations are relatively small [(1) C(10), 0.09, C(20) 0.18, (2) C(10) −0.04, C(20) 0.23 Å, respectively] as a direct result of the combined steric restraints imposed by hydrogen-bond formation and the cyclohexane ring. Hydrogen atoms of the adjacent methylene groups at C(12) and C(22) may well be a contributive restriction to the overall flexibility at C(10) and C(20), *viz.* torsion angles H–C(22)–C(20)–O(21) are close to 60°. Both N(7) and N(8) show very small deviations from the least-squares plane. Thus (1) and (2) possess an essentially planar phenylhydrazone fragment (A). The *para*-nitro-group in (2) is twisted out of the plane of the aromatic ring at an angle of 8.3°.

Turning to the dimedone-ring fragment of these derivatives it is perhaps pertinent to comment first on the structural parameters of the parent molecule itself, In the solid state, dimedone crystallises in the *trans*-enol form and these molecules are hydrogen bonded to each other *via* the hydrogen atom of the enol hydroxy and the oxygen atom of the carbonyl group to form infinite chains.[10,11] Ring dimensions are listed in Figure 3. C(13) is displaced 0.61 Å from the least-squares plane through C(22), C(12), C(20), C(9), and C(10) (using our crystallographic numbering system) and the oxygen atoms to give a cyclohexane-ring conformation described as an envelope. There is a clear differentiation between C–O bonds [keto C(20)–O(21) 1.246 Å, enol C(10)–O(11) 1.326 Å] and between the carbon–carbon ring dimensions [C(9)–C(10) 1.351 Å and C(9)–(20) 1.418 Å].



(I)



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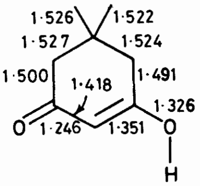

dimedone

FIGURE 3

There has been some structural change on forming the derivatives (1) and (2) (see Figure 3). The envelope conformation has been retained with C(13) and C(9) lying on the same side of the plane defined by C(10), C(20), C(12), and C(22). But there is a slightly more pronounced puckering of the cyclohexane ring at C(13). Deviations are C(9) 0.01, 0.02 and C(13) 0.68, 0.68 Å in structures (1) and (2), respectively. The two oxygen atoms can be regarded as coplanar with the C(10), C(20), C(12), and C(22) plane with deviations O(11) 0.07, −0.04 and O(21) 0.00, −0.04 Å for (1) and (2), respectively. Significantly each of the two C–O bond lengths in both (1) and (2) lie in the region expected for a keto linkage, *e.g.* C(20)–O(21) 1.214, 1.204 Å, C(10)–O(11), 1.223, 1.230 Å, thereby denying the presence of a large resonance contribution as in (B). Close similarities in the carbon–carbon distances C(20)–C(9) 1.457, 1.492 and C(9)–C(10) 1.457, 1.467 Å, respectively, for (1) and (2) lend further support to this view.

A search of the Cambridge Data Centre files for structural information on dimedone derivatives gave five examples of 5,5-dimethylcyclohexane-1,3-diones but all had very different bonding at the 2-position (or elsewhere) which made them unsuitable for direct comparison.

The 1,3-dioxan-4,6-dione ring system in the phenylhydrazone derivatives of Meldrum's acid [here the two methylene groups at C(22) and C(12) are replaced by oxygen atoms] adopts a similar, very shallow boat conformation with deviations with respect to the plane defined by C(10), O(12), C(20), and O(22) of C(9) 0.13, 0.08, 0.13 and C(13) 0.58, 0.56, 0.58 Å in structures (1), (2A), and (2B), respectively, of ref. 5. Clearly, the conformational difference of the 1,3-dioxan-4,6-dione and cyclohexane-1,3-diones is significant and must be due to interactions between the methylene hydrogens the latter.

The final point is that one of the reasons for determining the two structures (1) and (2) of similar type is that we can eliminate packing effects as being a contributary cause of the resulting dimedone ring conformation. The two structures have totally different space groups and intermolecular packing and thus we can state unequivocally that the present cyclohexane-ring envelope conformation is the most stable arrangement taking into account solely intramolecular forces. There are no intermolecular contacts of note in either structure.

EXPERIMENTAL

Compounds were isolated as yellow or orange crystalline solids in good yield following condensation reactions of the appropriate benzenediazonium salt with dimedone and

TABLE 4

Crystal data

	(1)	(2)
Formula	$C_{15}H_{18}N_2O_3$	$C_{14}H_{15}N_3O_4$
M	258.1	289.0
Crystal class	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$
Absences	$h0l$, $h + 1 = 2n + 1$ $0k0$, $k = 2n + 1$	
a(Å)	14.053(8)	7.20(1)
b(Å)	5.84(1)	13.45(1)
c(Å)	16.789(7)	7.45(1)
α(°)	(90)	97.97(5)
β(°)	98.9(1)	94.24(5)
γ(°)	(90)	98.29(5)
U(Å^3)	1 360.9	703.8
Z	4	2
μ(cm^{-1})	6.83	7.60
d_m (g cm^{-3})	1.43	1.48
d_c (g cm^{-3})	1.43	1.50
λ(Å)	0.7107	0.7107
F(000)	912	1 000
Crystal size (mm^3)	1.0 × 0.1 × 0.25	0.8 × 0.2 × 0.05
Rotation axis	b	a
$2\theta_{max.}$ (°)	50	50
No. of data	2 638	2 417
Criterion for data inclusion	$>1\sigma(I)$	$>2\sigma(I)$
No. of data in refinement	853	1 638
No. of parameters	193	210
R	0.087	0.078
R_w	0.091	0.083

cyclohexane-1,3-dione. The synthesis of cyclohexane-1,2,3-trione 2-(4-nitrophenylhydrazone) (9) is typical.

A solution of *p*-nitroaniline (13.8 g) in concentrated hydrochloric acid (25 cm^3) and water (25 cm^3) was cooled to 273 K and to it was added a chilled solution of sodium nitrite (6.9 g) in water (25 cm^3). The resulting solution of *p*-nitrobenzenediazonium chloride was filtered rapidly and added, with stirring, to a methanol (50 cm^3) solution of cyclohexane-1,3-dione (11.2 g) and sodium acetate (17.5 g) maintained at 273 K. After stirring the mixture for several hours, the product separated as an orange solid which was recrystallised from ethanol–dichloromethane (charcoal) as orange needles, m.p. 481—483 K. Analytical data for all compounds are listed in Table 1. Several of these have been mentioned previously by Garg *et al.*,[12] *viz.* (6)—(9). 90 MHz ^1H N.m.r. spectra were obtained using a Bruker WH90 instrument. ^{13}C N.m.r. spectra were obtained on a Bruker WH400 spectrometer operating at 100.6 MHz.

Crystal Structure Determinations.—The two crystals were mounted in turn on a Stoe STADI2 diffractometer and data was collected *via* variable-width *w* scan. Background counts were 20 s and the scan rate of 0.033 degree s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. Absorption and extinction corrections were not applied. Both structures were solved by the statistical method using SHELX 76. The structures were then refined by full-matrix least-squares with a weighting scheme that gave related values for $w\Delta^2$ over ranges of F_o and $\sin\theta/\lambda$. For both structures, this was $w = 1/[\sigma^2(F) + 0.003F^2]$ where $\sigma(F)$ was taken from counting statistics. Oxygen, nitrogen, and carbon atoms were refined anisotropically. Hydrogen atoms bonded to carbon were placed in tetrahedral or trigonal positions. Their thermal parameters were allowed to refine but those on the same atom were constrained to be equivalent. The hydrogen atom on N(7) was allowed to refine independently in (2). Hydrogen atoms on methyl groups

TABLE 5

Atomic co-ordinates ($\times 10^4$) for (1) with estimated deviations in parentheses

Atom	*x*	*y*	*z*
C(1)	2 004(6)	8 057(16)	6 006(6)
C(2)	1 437(6)	6 125(16)	6 137(5)
C(3)	1 150(6)	4 565(16)	5 542(5)
C(4)	1 428(5)	4 868(15)	4 796(5)
C(5)	1 976(6)	6 699(16)	4 631(5)
C(6)	2 260(6)	8 241(18)	5 233(5)
C(7)	2 322(7)	9 729(17)	6 681(6)
N(7)	1 120(5)	3 163(14)	4 201(4)
N(8)	1 399(4)	3 238(12)	3 494(4)
C(20)	1 451(5)	1 950(16)	2 174(5)
C(10)	505(6)	−302(14)	3 090(6)
C(12)	292(7)	−2 034(17)	2 433(5)
C(9)	1 112(5)	1 628(14)	2 943(5)
C(22)	1 159(5)	187(15)	1 525(5)
C(13)	208(5)	−1 046(16)	1 583(5)
C(30)	78(8)	−2 976(18)	957(7)
C(31)	−632(6)	629(17)	1 420(6)
O(11)	179(4)	−499(11)	3 720(4)
O(21)	1 956(4)	3 549(11)	2 042(4)

TABLE 6

Atomic co-ordinates ($\times 10^4$) for (2) with estimated deviations in parentheses

Atom	*x*	*y*	*z*
N(1)	3 149(4)	3 063(3)	−3 778(5)
O(1)	2 652(5)	2 152(3)	−3 800(4)
O(2)	3 829(5)	3 428(3)	−5 055(4)
C(1)	2 877(5)	3 756(3)	−2 152(5)
C(2)	2 291(5)	3 367(5)	−637(5)
C(3)	1 993(5)	4 022(3)	867(5)
C(4)	2 273(4)	5 064(3)	830(4)
C(5)	2 875(5)	5 448(3)	−699(5)
C(6)	3 171(5)	4 789(3)	−2 197(5)
N(7)	1 942(4)	5 708(2)	2 387(4)
N(8)	2 357(4)	6 695(2)	2 425(3)
C(9)	2 076(5)	7 337(2)	3 830(4)
C(20)	2 634(6)	8 428(3)	3 644(5)
C(22)	2 241(7)	9 203(3)	5 166(5)
C(13)	2 399(5)	8 889(2)	7 054(5)
C(12)	1 048(5)	7 881(3)	6 997(5)
C(10)	1 273(4)	7 053(3)	5 475(5)
O(21)	3 352(6)	8 672(2)	2 329(4)
C(30)	4 413(5)	8 742(3)	7 612(6)
C(31)	1 795(7)	9 707(3)	8 435(6)
O(11)	758(3)	6 156(2)	5 611(3)

TABLE 7

Molecular dimensions (Å and °) in (1) and (2)

	(1)	(2)
C(1)–C(7)	1.510(12)	
C(1)–N(1)		1.466(4)
N(1)–O(2)		1.231(5)
N(1)–O(1)		1.223(5)
C(1)–C(2)	1.418(12)	1.376(5)
C(1)–C(6)	1.404(11)	1.380(5)
C(2)–C(3)	1.366(11)	1.377(5)
C(3)–C(4)	1.380(12)	1.391(5)
C(4)–C(5)	1.371(12)	1.387(5)
C(4)–N(7)	1.429(10)	1.405(4)
C(5)–C(6)	1.365(12)	1.375(4)
N(7)–N(8)	1.307(9)	1.314(4)
N(8)–C(9)	1.336(9)	1.308(4)
C(10)–C(9)	1.457(11)	1.467(5)
C(20)–C(9)	1.457(11)	1.492(5)
C(10)–C(12)	1.492(12)	1.510(5)
C(10)–O(11)	1.223(10)	1. 230(4)
C(12)–C(13)	1.527(12)	1.545(5)
C(22)–C(13)	1.534(11)	1.525(5)
C(13)–C(30)	1.532(13)	1.527(5)
C(13)–C(31)	1.524(12)	1.533(5)
C(20)–C(22)	1.509(11)	1.502(4)
C(20)–O(21)	1.214(10)	1.204(4)
C(6)–C(1)–N(1)		118.8(3)
C(2)–C(1)–N(1)		119.9(3)
C(1)–N(1)–O(1)		117.9(3)
C(1)–N(1)–O(2)		118.4(3)
O(1)–N(1)–O(2)		123.7(3)
C(2)–C(1)–C(7)	123.8(9)	
C(6)–C(1)–C(7)	123.8(9)	
C(2)–C(1)–C(6)	115.8(9)	121.5(3)
C(1)–C(2)–C(3)	121.7(8)	119.3(3)
C(2)–C(3)–C(4)	119.0(9)	119.6(3)
C(3)–C(4)–C(5)	122.1(8)	120.5(3)
C(3)–C(4)–N(7)	116.5(8)	118.0(3)
C(5)–C(4)–N(7)	121.4(8)	121.5(3)
C(4)–C(5)–C(6)	118.3(8)	119.5(3)
C(1)–C(6)–C(5)	123.1(9)	119.5(3)
C(4)–N(7)–N(8)	120.7(8)	118.43(28)
N(7)–N(8)–C(9)	120.3(7)	121.51(28)
N(8)–C(9)–C(10)	123.3(7)	125.1(3)
N(8)–C(9)–C(20)	114.7(7)	114.3(3)
C(20)–C(9)–C(10)	122.0(8)	120.65(29)
C(12)–C(10)–C(9)	117.0(8)	119.1(3)
C(9)–C(10)–O(11)	121.9(8)	120.8(3)
C(12)–C(10)–O(11)	121.1(8)	120.1(3)
C(10)–C(12)–C(13)	114.4(8)	114.7(3)
C(12)–C(13)–C(22)	107.2(7)	108.04(28)
C(12)–C(13)–C(30)	110.3(8)	109.7(3)
C(22)–C(13)–C(30)	108.3(7)	111.0(3)
C(12)–C(13)–C(31)	110.8(7)	109.0(3)
C(22)–C(13)–C(31)	110.2(7)	109.3(3)
C(30)–C(13)–C(31)	110.0(7)	109.9(3)
C(9)–C(20)–C(22)	117.6(7)	119.1(3)
C(9)–C(20)–O(21)	122.8(8)	121.4(3)
C(22)–C(20)–O(21)	119.6(8)	121.8(3)
C(20)–C(22)–C(13)	114.5(7)	115.1(3)

TABLE 8

Least-squares planes. Distances of atoms (Å) from the plane of atoms C(n), n = 1—6 are given. Standard deviations of atoms from the planes at 0.01 Å

	(1)	(2)
C(1)	−0.00	−0.00
C(2)	0.00	−0.00
C(3)	−0.00	0.00
C(4)	0.00	−0.00
C(5)	−0.00	0.00
C(6)	0.00	−0.00
N(1)		−0.07
O(1)		0.09
O(2)		−0.30
C(7)	0.02	
N(7)	0.02	−0.01
N(8)	0.11	0.11
C(9)	0.13	0.13
C(10)	0.09	−0.04
C(20)	0.18	0.23

Angle of intersection between the phenyl-ring plane and the nitro-group in (2) is 8.3(1)°.

Dimedone fragment, plane 2 consists of atoms C(10), C(20), C(12), and C(22) which are coplanar

	(1)	(2)
C(9)	0.01	0.02
C(13)	0.68	0.68
O(11)	0.07	−0.04
O(21)	0.00	−0.04

were refined as rigid groups with a common thermal parameter. Scattering factors were taken from International Tables.[13] Calculations were made using SHELX 76 on the CDC 7600 computer at the University of Manchester Computer Centre.[14] Crystal data and refinement details are given in Table 4. Atomic co-ordinates are given in Tables 5—7. Details of interatomic distances and angles are listed in Table 8. The anisotropic thermal parameters, observed and calculated structure factors, and hydrogen atom positions are given in Supplementary Publication No. SUP 23344 (17 pp.).*

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2,* 1981, Index Issue.

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