Structural Investigations of Ylides. Part II.† Crystal and Molecular Structure of (+)-3-Diazocamphor

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The title compound crystallises in the monoclinic system, space group $P2_1$, with $Z = 2$ in a unit cell of dimensions $a = 7{\cdot}119(2)$, $b = 7{\cdot}466(2)$, $c = 9{\cdot}279(2)$ Å, $\beta = 91{\cdot}75(2)°$. The structure was solved from *X*-ray diffractometer data by comparison with the structures of certain other isomorphous (+)-camphor derivatives, and was refined by least-squares techniques to *R* 0·087 for 661 independent reflexions. The results of the analysis indicate that stabilisation of diazoketones *via* the diazo-function occurs to an extent similar to that which would be expected for the less stable diazoalkanes, with the additional stability resulting from small contributions from the enolate forms of diazoketones.

DIAZOKETONES (I; a—c) and diazoalkanes (II; a—e) may both be regarded as ylides,[1] the enhanced stability of the former compounds over the latter being considered to arise from contributions in which the negative charge is delocalised into the enolate moiety (I; b),[2,3] although in diazoketones both the diazo- and enolate functions can plausibly compete to delocalise the negative charge. Evidence for the stabilisation of other first-row ylides *via* delocalisation into enolate groupings has already been found,[4,5] and in addition, variable-temperature n.m.r. studies of diazo-ketones, -aldehydes and -esters, have shown that both the *cis*- and *trans*-forms [with respect to the C(1)–C(2) bond in (I)] may exist in solution.[6]

As part of a study of ylides of first-row elements,[4] and in an attempt to investigate the extent to which the

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† Part I, A. F. Cameron, N. J. Hair, and D. G. Morris, *J.C.S. Perkin II*, 1972, 1071.

[1] A. W. Johnson, 'Ylid Chemistry,' Academic Press, New York, 1966.

[2] R. Huisgen, *Angew. Chem.*, 1955, **67**, 439.

[3] A. Ledwith and G. W. Cowell, *Quart. Rev.*, 1970, **24**, 119.

[4] A. F. Cameron, N. J. Hair, D. G. Morris, and D. M. Hawley, *Chem. Comm.*, 1971, 725.

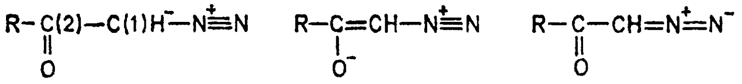
[5] N. A. Bailey, S. E. Hull, G. F. Kersting, and J. Morrison, *Chem. Comm.*, 1971, 1429.

[6] F. Kaplan and G. K. Meloy, *J. Amer. Chem. Soc.*, 1966, **88**, 950.

resonance form (I; b) is involved in the stabilisation of diazoketones, we have determined the crystal structure of (+)-3-diazocamphor (III), an all-*cis* diazoketone which contains a nonaromatic carbocyclic residue.

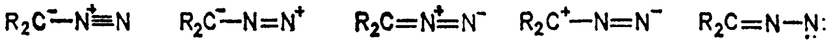
EXPERIMENTAL

Crystals of (III) were prepared by the reaction of camphorquinone-3-hydrazone [obtained from (+)-camphor] with mercuric oxide, and recrystallised from light petroleum as yellow needles (m.p. 76 °C).



$\mathrm{R{-}\underset{\underset{O}{\|}}{C}(2){-}C(1)H^{-}{-}\overset{+}{N}{\equiv}N}$ (a) $\mathrm{R{-}\underset{\underset{O^{-}}{|}}{C}{=}CH{-}\overset{+}{N}{\equiv}N}$ (b) $\mathrm{R{-}\underset{\underset{O}{\|}}{C}{-}CH{=}\overset{+}{N}{=}N^{-}}$ (c)

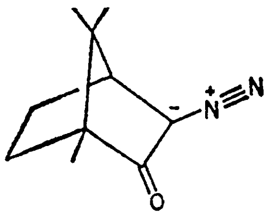
(I)



$\mathrm{R_2C^{-}{-}\overset{+}{N}{\equiv}N}$ (a) $\mathrm{R_2C^{-}{-}N{=}N^{+}}$ (b) $\mathrm{R_2C{=}\overset{+}{N}{=}N^{-}}$ (c) $\mathrm{R_2C^{+}{-}N{=}N^{-}}$ (d) $\mathrm{R_2C{=}N{-}\ddot{N}:}$ (e)

(II)

Crystal Data.—$C_{10}H_{14}N_2O$, $M = 178{\cdot}2$, Monoclinic, $a = 7{\cdot}119(2)$, $b = 7{\cdot}466(2)$, $c = 9{\cdot}279(2)$ Å, $\beta = 91{\cdot}75(2)°$ $U = 492{\cdot}9$ Å^3, $D_m = 1{\cdot}18$ (by flotation in aqueous potassium iodide), $Z = 2$, $D_c = 1{\cdot}20$, $F(000) = 192$. Space group, $P2_1$ (C_2^2). Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; μ(Mo-K_α) = 0·85 cm^{-1}.



(III)

Crystallographic Measurements.—The unit-cell dimensions were initially determined from oscillation and Weissenberg photographs taken with Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation, and from precession photographs taken with Mo-K_α radiation, and were subsequently refined by least-squares calculations before the diffractometer data collection. Space group $P2_1$ was indicated both from systematic absences in the 0*k*0 spectra and also by the known optical activity of (III).

A suitable crystal (*ca.* 0·6 × 0·3 × 0·1 mm) was sealed in a quartz capillary tube since the crystals showed a tendency to evaporate in the atmosphere, and intensity measurements were made on a Hilger and Watts Y 290 diffractometer by use of zirconium filtered Mo-radiation. Within the range $0 < 2\theta \leqslant 60°$, 661 independent reflexions having $I > 3\sigma(I)$ were recorded, and the appropriate Lorentz and polarisation corrections were applied. Absorption effects were considered small and were ignored.

Structure Determination.—The data contained in Table 1 suggest that the present compound is isomorphous with certain other camphor derivatives, the structures of which have been previously determined.[7,8] It was therefore assumed that the crystalline arrangement and molecular geometry of the $C_{10}O$ fragment of (+)-3-bromocamphor[8] would represent a reasonable model for the structure of the same portion of the present molecule, and the quoted values for the co-ordinates of the carbon and oxygen atoms were used in a preliminary structure-factor and electron-density calculation which revealed the two nitrogen atom positions of (III). Two further rounds of structure-factor and electron-density calculations effected a preliminary refinement. In all the previous calculations an overall value of 0·05 Å^2 for U_{iso} was assumed, and after each calculation the data were placed on an approximate absolute scale by equating $k\Sigma|F_o|$ and $\Sigma|F_c|$.

Structure Refinement.—The refinement of positional vibrational [anisotropic after cycle (6)] and scale parameters by full-matrix least-squares calculations, converged after 13 cycles when R was 0·087 and $R'(=\Sigma w\Delta^2|\Sigma w|F_o|^2)$ was 0·0117. After cycle (4), the positions of the five non-methyl hydrogen atoms were determined from a difference synthesis, and their contributions were included [but not refined until after cycle (10)] in all subsequent cycles. An overall isotropic vibrational parameter U_{iso} 0·06 Å^2 was assumed for all five hydrogen atoms, and was not allowed to vary in any of the refinement cycles.

TABLE 1

Crystallographic data for various camphor derivatives

Derivative	*a*	*b*	*c*	β	*U*	Space group
3-CN [a]	7·13 Å	7·44	9·40	94° 30′	496 Å^3	$P2_1$
3-Cl [a]	7·25	7·51	9·04	93° 15′	491	$P2_1$
3-Br [a]	7·38	7·57	9·12	94° 0′	508	$P2_1$
(+)-3-Br [b]	7·36	7·59	9·12	94° 6′	508	$P2_1$
(+)-3-Diazo- [c]	7·119	7·466	9·279	91° 45′	493	$P2_1$

[a] Ref. 7. [b] Ref. 8. [c] Present work.

During the initial stages of the refinement, all reflexions were assigned unit weights, but in later cycles a weighting scheme of the form $|F_o| \leqslant p_1$, $\sqrt{w} = 1$; $|F_o| > p_1$, $\sqrt{w} = p_1/|F_o|$ was used. The parameter p_1 (final value 10) was adjusted in accordance with an $|F_o|$ analysis of $w\Delta^2$.

At the conclusion of the refinement, a difference-Fourier synthesis and electron-density distribution were calculated, neither of which revealed any gross errors in the structure, and which failed to resolve the methyl hydrogen atoms. The difference-Fourier synthesis did, however, contain peaks of residual electron density (0·4—0·6 eÅ^{-3}) roughly centred on the non-hydrogen atom positions. This may possibly be interpreted either as a failure of the present model to

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[7] E. H. Wiebenga and C. J. Krom, *Rec. Trav. Chim.*, 1946, **65**, 663.

[8] F. H. Allen and D. Rogers, *J. Chem. Soc.* (*B*), 1971, 632.

account for a highly anisotropic motion of the molecule (the crystal tended to evaporate at room temperature), or may reflect the effects of radiation damage to the crystals. Similar evidence of radiation damage has been observed for (+)-3-bromocamphor,[8] and for the diazo-compound, 2-bromodiazofluorene.[9]

TABLE 2

(*a*) Fractional co-ordinates

	x/a	y/b	z/c
O(1)	0·3929(7)	0·2862	0·0723(6)
N(1)	0·7263(8)	0·3047(15)	−0·1045(6)
N(2)	0·7214(11)	0·3142(20)	−0·2255(7)
C(1)	0·6290(8)	0·3172(13)	0·2708(6)
C(2)	0·5551(9)	0·2939(13)	0·1165(7)
C(3)	0·7252(9)	0·2913(13)	0·0348(7)
C(4)	0·8912(9)	0·3132(14)	0·1392(7)
C(5)	0·8882(13)	0·5099(14)	0·1923(9)
C(6)	0·7040(13)	0·5129(12)	0·2770(9)
C(7)	0·8153(8)	0·2061(10)	0·2704(7)
C(8)	0·7816(15)	0·0044(15)	0·2427(10)
C(9)	0·9387(12)	0·2262(15)	0·4091(8)
C(10)	0·4834(11)	0·2645(19)	0·3844(9)
H(41)	1·010(13)	0·257(15)	0·094(9)
H(51)	0·996(13)	0·526(15)	0·254(10)
H(52)	0·842(13)	0·602(17)	0·113(10)
H(61)	0·631(14)	0·568(16)	0·212(10)
H(62)	0·736(13)	0·537(15)	0·378(10)

(*b*) Anisotropic temperature factors * (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O(1)	0·0430	0·1475	0·0699	0·0251	−0·0217	0·0030
N(1)	0·0537	0·1065	0·0396	−0·0034	0·0043	0·0247
N(2)	0·0815	0·1766	0·0427	0·0065	0·0179	0·0342
C(1)	0·0401	0·0659	0·0391	−0·0038	0·0084	0·0072
C(2)	0·0417	0·0650	0·0472	0·0018	0·0048	−0·0090
C(3)	0·0498	0·0655	0·0406	0·0072	−0·0000	−0·0026
C(4)	0·0412	0·0750	0·0414	−0·0097	0·0068	−0·0149
C(5)	0·0787	0·0679	0·0564	0·0143	−0·0063	−0·0510
C(6)	0·0879	0·0390	0·0643	0·0015	−0·0020	0·0105
C(7)	0·0371	0·0357	0·0433	−0·0113	−0·0160	0·0128
C(8)	0·0988	0·0516	0·0836	−0·0153	−0·0221	0·0278
C(9)	0·0590	0·0879	0·0562	0·0337	−0·0329	−0·0081
C(10)	0·0531	0·1332	0·0559	0·0070	0·0350	0·0179

Mean estimated standard deviations (Å^2)

	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{31}$	$2U_{12}$
O	0·0025	0·0068	0·0033	0·0097	0·0046	0·0093
N	0·0039	0·0083	0·0029	0·0103	0·0054	0·0123
C	0·0041	0·0052	0·0037	0·0083	0·0064	0·0086

* The anisotropic temperature factor is in the form: $\exp[-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{31}lhc^*a^* + 2U_{12}hka^*b^*)]$.

In all structure-factor calculations, the atomic scattering factors used were taken from ref. 10. Values of observed and calculated structure factors are listed in Supplementary Publication No. SUP 20406 (3 pp., 1 microfiche).[*,1] Table 2 contains the final fractional co-ordinates and anisotropic thermal parameters, while Table 3 contains all bond lengths, valency angles, and pertinent intra- and inter-molecular non-bonded distances. The appropriate estimated standard deviations derived from the inverse of the least-squares normal-equation matrix, are included in Tables 2 and 3. The mean σ for C–O, C–N, C–C, C–H, and N–N bonds are 0·008, 0·008, 0·011, 0·10 and 0·008 Å

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bonded distances

O(1)–C(2)	1·215(8)	C(3)–C(4)	1·514(9)
N(1)–N(2)	1·125(8)	C(4)–C(5)	1·549(14)
N(1)–C(3)	1·296(8)	C(4)–C(7)	1·566(10)
C(1)–C(2)	1·520(9)	C(5)–C(6)	1·549(13)
C(1)–C(6)	1·556(13)	C(7)–C(8)	1·546(13)
C(1)–C(7)	1·565(10)	C(7)–C(9)	1·543(10)
C(1)–C(10)	1·551(10)	Mean C–H	0·98(10)
C(2)–C(3)	1·448(9)		

(*b*) Interbond angles (°)

N(2)–N(1)–C(3)	177·8(8)	C(2)–C(3)–C(4)	108·2(5)
C(2)–C(1)–C(6)	104·5(7)	C(3)–C(4)–C(5)	106·7(7)
C(2)–C(1)–C(7)	101·9(5)	C(3)–C(4)–C(7)	99·3(5)
C(2)–C(1)–C(10)	113·1(6)	C(5)–C(4)–C(7)	103·2(6)
C(6)–C(1)–C(7)	102·0(6)	C(4)–C(5)–C(6)	101·3(7)
C(6)–C(1)–C(10)	116·6(8)	C(1)–C(6)–C(5)	105·2(7)
C(7)–C(1)–C(10)	116·8(7)	C(1)–C(7)–C(4)	92·5(5)
O(1)–C(2)–C(1)	128·4(6)	C(1)–C(7)–C(8)	112·9(6)
O(1)–C(2)–C(3)	128·7(6)	C(1)–C(7)–C(9)	114·1(6)
C(1)–C(2)–C(3)	102·9(5)	C(4)–C(7)–C(8)	115·1(6)
N(1)–C(3)–C(2)	123·4(6)	C(4)–C(7)–C(9)	113·4(6)
N(1)–C(3)–C(4)	127·0(6)	C(8)–C(7)–C(9)	108·4(7)

(*c*) Intramolecular non-bonded distances (Å) <3·5 Å

O(1) ··· N(1)	2·93	C(2) ··· C(8)	2·92
O(1) ··· C(6)	3·33	C(3) ··· C(6)	2·80
O(1) ··· C(10)	2·95	C(3) ··· C(8)	2·90
N(1) ··· C(5)	3·33	C(5) ··· C(9)	2·94
N(2) ··· C(2)	3·42	C(6) ··· C(9)	2·96
C(1) ··· C(4)	2·26	C(8) ··· C(10)	3·19
C(2) ··· C(5)	2·94	C(9) ··· C(10)	3·26

(*d*) Intermolecular distances (Å)

O(1) ··· N(1^{I})	3·71	N(2) ··· C(6^{I})	3·79
O(1) ··· N(1^{II})	3·98	N(2) ··· C(8^{II})	3·85
O(1) ··· N(2^{I})	3·89	N(2) ··· C(9^{IV})	3·83
O(1) ··· C(3^{I})	3·91	N(2) ··· C(10^{II})	3·93
O(1) ··· C(3^{II})	3·98	N(2) ··· C(10^{IV})	3·97
O(1) ··· C(4^{III})	3·65	C(5) ··· C(8^{V})	3·80
O(1) ··· C(5^{I})	3·74	C(6) ··· C(8^{V})	3·73
O(1) ··· C(6^{I})	3·87	C(6) ··· C(10^{VI})	3·93
O(1) ··· C(8^{II})	3·54	C(9) ··· C(10^{VII})	3·90

Roman numerals as superscripts refer to the following equivalent positions:

I $1 - x, -\frac{1}{2} + y, -z$
II $1 - x, \frac{1}{2} + y, -z$
III $-1 + x, y, z$
IV $x, y, -1 + z$
V $x, 1 + y, z$
VI $1 - x, \frac{1}{2} + y, 1 - z$
VII $1 + x, y, z$

TABLE 4

Equations of best least-squares planes in the form $AX' + BY' + CZ' = D$ where X', Y', and Z' are co-ordinates in Å, and in square bracket deviations (Å) of relevant atoms from the planes

	A	B	C	D
Plane (1): C(1)—(4) [C(1) −0·001, C(2) 0·001, C(3) −0·001, C(4) 0·001, O(1) 0·045, N(1) 0·231, N(2) 0·420]	−0·0541	0·9932	−0·1033	1·8648
Plane (2): C(1), C(4)—(6) [C(1) −0·013, C(4) 0·013, C(5) −0·019, C(6) 0·019]	−0·5358	0·2142	−0·8092	−3·7355
Plane (3): C(1)—(3), O(1) [C(1) 0·004, C(2) −0·013, C(3) 0·004, O(1) 0·006]	−0·0342	0·9946	−0·0976	1·9669
Plane (4): C(2)—(4), N(1) [C(2) −0·021, C(3) 0·071, C(4) −0·021, N(1) −0·028]	−0·0602	0·9982	0·0001	1·9309

Dihedral angles (°) between planes

(1)–(2)	69·4
(3)–(4)	5·8

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[*] For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

[9] A. Griffiths and R. Hine, *Acta Cryst.*, 1970, *B*26, 34.

[10] ' International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

respectively, and for valency angles 0·6°. These are probably best regarded as minimum values. Details of least-squares planes calculated for various portions of the molecular framework are given in Table 4. The atomic numbering system used, and the molecular packing viewed along the *a* axis, are shown in Figures 1 and 2 respectively.

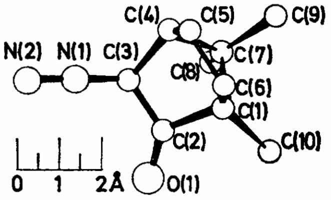


FIGURE 1 A view of the molecule showing the atomic numbering (hydrogens are numbered as the carbon atoms to which they are bonded)

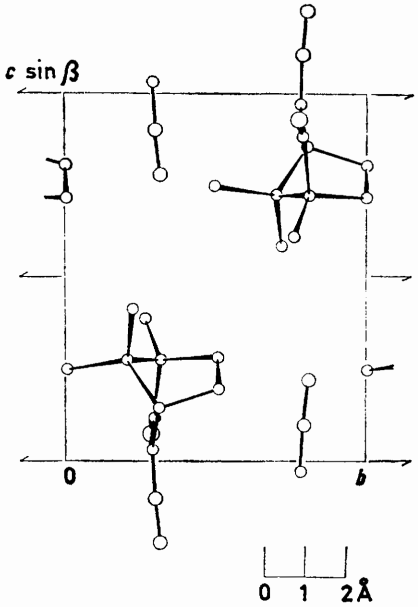
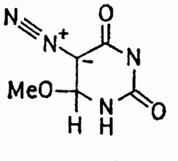


FIGURE 2 A projected view of the molecular packing

DISCUSSION

The analysis of (III) has not only confirmed that the crystal structure of (+)-3-diazocamphor is isomorphous with the structures of the other three camphor derivatives listed in Table 1, but has also yielded information as to the bonding and stabilisation which may be expected for diazoketones.

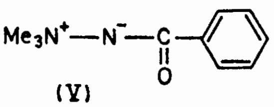
Examination of the geometry of the diazo-group reveals that the atoms C(3), N(1), and N(2) have an almost linear arrangement [angle C(3)–N(1)–N(2) 177·8(8)°], the C(3)–N(1) and N(1)–N(2) bonds having lengths of 1·296(8) and 1·125(8) Å respectively. These values are comparable to the corresponding lengths of 1·332 and 1·113 Å quoted recently for another diazoketone, 5-diazo-6-methoxy-(6*H*)-uracil (IV).[11] However, to assess the importance of the diazo-function in the stabilisation of diazoketones, comparisons must be made with the corresponding data for diazoalkanes. Thus diazomethane possesses a linear structure with C–N and N–N bonds of 1·32 and 1·12 Å respectively,[12] while values of 1·32(3) and 1·12(3) Å are found for the corresponding bonds of 2-bromo-9-diazofluorene.[9] From such comparisons it would appear that the diazo-groupings in both diazo-ketones and -alkanes are very similar, which suggests comparable electronic structures within these residues of the different molecules. A



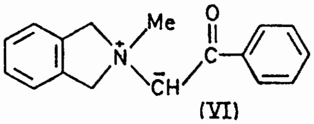
(IV)

possible conclusion, therefore, is that stabilisation of the negative charge in the diazoketone (III) *via* delocalisation into the diazo-moiety, has occurred to an extent similar to that which would be expected for diazoalkanes.

In support of this conclusion, the geometry of the C(3)–C(2)–O(1) system would indicate that the keto-form (I; a) predominates over the enolate (I; b). The carbonyl bond [1·215(8) Å] is not significantly different from similar bonds in aliphatic ketones,[13] and although it has been shown that the length of a carbonyl bond is relatively insensitive to changes in conjugation,[14,15] slight, but significant lengthening has been observed both in the *N*-ammonio amidate (V) [4] and the ammonium ylide (VI) [5] [1·243(5) and 1·27 Å respectively]. We may infer, therefore, that only minor delocalisation of the negative charge on the oxygen atom O(1) of (III) has occurred. Moreover,



(V)



(VI)

$\mathrm{Me_3N^+{-}N^-{-}NO_2}$

(VII)

the C(2)–C(3) bond [1·448(9) Å] distance may be compared with the value calculated (1·476 Å) for a single bond between two sp^2-hybridised carbons,[16] and with the experimental values (1·483 and 1·475 Å) found for butadiene [17] and 1,3-cyclo-octadiene.[18] The values of 1·448(9) in (III), and 1·436 Å in (IV), are thus only slightly shortened to an extent consistent with the

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[11] D. J. Abraham, T. G. Cochran, and R. D. Rosenstein, *J. Amer. Chem. Soc.*, 1971, **93**, 6279.

[12] A. P. Cox, L. F. Thomas, and J. Sheridan, *Nature*, 1958, **181**, 1000.

[13] *Chem. Soc. Special Publ.*, No. 18, 1965.

[14] C. J. Fritchie and J. L. Wells, *Chem. Comm.*, 1968, 917.

[15] H. Bärnighausen, F. Jellinek, J. Munnik, and A. Vos, *Acta Cryst.*, 1963, **16**, 471.

[16] M. J. S. Dewar and H. M. Schmeising, *Tetrahedron*, 1959, **5**, 166.

[17] A. Almenningen, O. Bastiansen, and M. Traettenberg, *Acta Chem. Scand.*, 1958, **12**, 221.

[18] M. Traettenberg, *Acta Chem. Scand.*, 1970, **24**, 2285.

introduction of only a limited amount of double-bond character into the C(2)–C(3) bond in (III) and the corresponding bond in (IV). This view is further supported by comparison with the corresponding bond [1·36 Å] in the ammonium ylide (VI),[5] where charge delocalisation to produce an enolate form has definitely occurred.

To the extent, therefore, that bond extension [C(2)–O(1)] and bond contraction [C(2)–C(3)] within the C(2)–C(3)–O(1) system may be taken as a measure of the delocalisation of the negative charge within this part of the molecule, we may possibly conclude, since both diazo-ketones and -alkanes are apparently stabilised to a similar extent *via* the diazo-functions, that it is the minor additional delocalisation into the enolate groupings of diazoketones which is, at least in part, responsible for their enhanced stability. Further support for at least a minor contribution from the enolate (I; b) form in diazoketones, is provided by comparison of the i.r. carbonyl frequency $\nu_{max.}$ (CCl_4) 1692 cm^{-1} for (III) with the value of $\nu_{max.}$ 1751 cm^{-1} for norcamphor.[19]

We have previously discussed the *cis*-conformations common to the first-row ylides (V), which is carbonyl stabilised, and (VII), which is stabilised by the nitro-group.[4] Both compounds show geometrical evidence of slight delocalisation of the negative charge on the oxygen atoms, and the effect of the *cis*-conformations is to produce short $N^{+} \cdots O^{\delta-}$ intramolecular contacts of 2·74 (V) and 2·65 Å (VII). Similar conclusions result from the study of (VI).[5] Although (+)-3-diazocamphor is a first-row ylide, the constraints placed by the bicyclic skeleton on the overall conformation, render difficult any direct comparisons with the conformations of the other molecules, since the diazo- and keto-functions are in this case restricted to be *cis*. Nevertheless, the dihedral angle between the planes of atoms [C(1), C(2), C(3), O(1)] and [C(2), C(3), C(4), N(1)] is almost 6°, indicating a larger degree of twist about the C(2)–C(3) bond than is observed for the corresponding bonds both in (V) (2°) and in (VII) (0°). Also the N(1) ··· O(1) separation (2·93 Å) in (III) is significantly longer than the corresponding distances in the other two compounds.

Other dimensions in the bicyclo[2,2,1]heptyl system compare well with literature values for similar bond types. The mean valency angle within the bicyclic system is 101·8°, similar to values quoted in previous studies,[20] while the C(1)–C(7)–C(4) [92·5(5)°] angle is in good agreement with values obtained for other norbornane derivatives.[8] The molecules in the crystal exhibit neither abnormally short intra- nor intermolecular distances, indicating that the crystal-packing is determined by van der Waals forces.

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