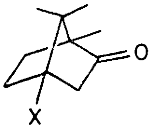
# Carbon-13 Chemical Shifts and Substituent Effects in 4-Substituted Camphors, *N*-Nitrocamphorimines, and Diazocamphors

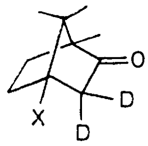
By **David G. Morris** * and **A. Malcolm Murray**, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ

Carbon-13 chemical shifts of a series of 4-substituted camphors (1)—(11) are reported, and are considered in relation to substituent effects and related systems. Electron-withdrawing substituents cause high-field shifts of the carbonyl carbon [C(2)] signal, whose shieldings correlate empirically with the linear free energy parameter, $\sigma_I$. In the derived nitroimines (13)—(17), where no evidence is found for geometrical isomerism at the carbon–nitrogen double bond, C(2) is shielded by *ca.* 30 p.p.m. with respect to the corresponding camphor. In compounds (2), (5), and (11) and norcamphor, deuteriation at C(3) brings about high-field isotope shifts at certain carbon atoms. Carbon-13 and nitrogen-15 chemical shifts of diazocamphors and 9-diazofluorene are reported and discussed.

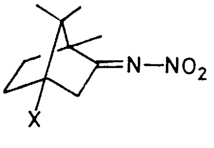
BRIDGEHEAD-SUBSTITUTED bicyclic and tricyclic ring systems of well defined geometry are of considerable interest for a study of substituent dependence of $^{13}$C chemical shifts. At present such data are available for bridgehead-substituted adamantanes [1,2] and bicyclo[2.2.2]octanes,[3,4] in addition to 4-substituted tricyclenes,[4] 1-substituted camphenes,[5] and certain 1-substituted bicyclo[3.2.1]octanes.[6] From a study of substituent effects on $^{13}$C chemical shifts it is possible to derive empirical correlations concerning the magnitude of shifts at particular carbon atoms which may be both of predictive value in related systems, and also of use in providing an improved understanding of the relationship with both structural and electronic properties of molecules. A review of factors affecting chemical shifts has recently appeared.[7]



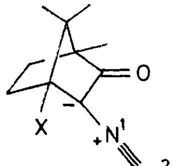
(1) X = H
(2) X = Me
(3) X = $NH_2$
(4) X = OH
(5) X = Cl
(6) X = Br
(7) X = $CO_2H$
(8) X = $CO{\cdot}NH_2$
(9) X = $CO_2Me$
(10) X = COMe
(11) X = $NO_2$
(12) X = $CH_2D$



(2a) X = Me
(5a) X = Cl
(11a) X = $NO_2$



(13) X = H
(14) X = Me
(15) X = Cl
(16) X = $CO_2H$
(17) X = $NO_2$



(18) X = H
(19) X = Me

In the present work we have examined $^{13}$C chemical shifts of the 4-substituted camphors (1)—(11) and a representative number of the derived *N*-nitrocamphorimines (13)—(17). We have also considered the $^{13}$C spectra of the diazocamphors (18) and (19), together with the $^{15}$N spectra of (18) and 9-diazofluorene. Carbon-13 chemical shifts of the camphors (1)—(11) and the derived substituent chemical shifts are given respectively, in Tables 1 and 2.

## RESULTS AND DISCUSSION

Assignments of $^{13}$C absorptions are supported by proton-decoupled off-resonance spectra. Although the C(3) absorption in compounds (1)—(11) is generally sufficiently downfield from the off-resonance triplet absorptions for C(5) and C(6) as to provide unambiguous assignment, further support is provided by the absence of additional fine structure in the off-resonance signal for C(3) as compared with those for C(5) and C(6), in accord with the findings of Grutzner [8] for related systems. Data previously available were also useful, as in assignment of the substituent-bearing carbon atom C(4). The assignment of the C(4) signals for (7) and (9) is complicated by the occurrence within 10 p.p.m. of three quaternary carbon resonances. However the assignment (Table 1) is supported by the general observation that in the camphors (1)—(11) C(4) absorbs 0—2 p.p.m. to lower field than C(4) in 4-substituted tricyclenes [4] and 3—5 p.p.m. to higher

---

[1] T. Pehk, E. Lippmaa, V. V. Sevostjanova, M. M. Krayushkin, and A. I. Tarasova, *Org. Magnetic Resonance*, 1971, **3**, 783.

[2] G. E. Maciel, H. C. Dorn, R. L. Greene, W. A. Kleschick, M. R. Peterson, and G. H. Wahl, *Org. Magnetic Resonance*, 1974, **6**, 178.

[3] G. E. Maciel and H. C. Dorn, *J. Amer. Chem. Soc.*, 1971, **93**, 1268.

[4] D. G. Morris and A. M. Murray, *J.C.S. Perkin II*, 1975, 734.

[5] D. G. Morris and A. M. Murray, *J.C.S. Perkin II*, 1975, 539.

[6] A. N. Kalinichenko, A. A. Bobyleva, N. A. Belikova, A. F. Plate, T. I. Pekhk, and E. T. Lippmaa, *J. Org. Chem., U.S.S.R.*, 1974, **10**, 1459.

[7] N. K. Wilson and J. B. Stothers, *Topics Stereochem.*, 1973, **8**, 1.

[8] J. B. Grutzner, *J.C.S. Chem. Comm.*, 1974, 64.

field than the corresponding carbon atom, C(1), in 1-substituted tricyclenes.[5] Although reasons for variation of the shielding of substituent-bearing carbon are uncertain, the effect has been noted in a wider context.[9]

The response of α-shifts for C(4) and β-shifts for C(3), C(5), and C(7) to substituent variation in the series (1)—(11) closely parallels that of the corresponding carbon atoms in 4-substituted tricyclenes.[4] That the smaller β-shifts for C(3) with respect to C(5) are probably not due to differential ' γ-effect ' shielding [10] from C(8) and C(9) on account of ring distortion [11] is indicated by the similar respective C(3) and C(5) β-shifts observed in the particular cases of (2) and 4-methylnorcamphor.[12]

TABLE 1

$^{13}$C Chemical shifts (p.p.m. from $Me_4Si$) of 4-substituted camphors

| Compd. | X | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) | C(9) | C(10) | C(11) | C(12) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (1) | H | 57.4 | 218.4 | 43.1 | 43.2 | 27.0 | 29.9 | 46.6 | 19.7 | 19.1 | 9.2 | | |
| (2) | Me | 59.60 | 218.71 | 48.97 | 45.45 | 34.32 | 29.59 | 48.08 | 17.45 | 15.78 | 10.04 | 15.42 | |
| (2a) | Me[3,3-$^2H_2$] | 59.61 | 218.83 | 48.03 | 45.31 | 34.25 | 29.61 | 48.06 | 17.44 | 15.77 | 10.00 | 15.40 | |
| (3) | $NH_2$ | 59.0 | 215.9 | 49.0 | 61.9 | 34.6 | 28.5 | 48.2 | 16.9 | 15.0 | 10.4 | | |
| (4) | OH | 58.5 | 215.7 | 48.1 | 79.7 | 33.2 | 27.9 | 48.1 | 17.0 | 15.1 | 10.0 | | |
| (5) | Cl | 57.88 | 212.85 | 50.84 | 70.09 | 36.27 | 28.56 | 50.56 | 17.25 | 15.78 | 10.29 | | |
| (5a) | Cl[3,3-$^2H_2$] | 57.88 | 212.86 | 50.22 | 69.94 | 36.17 | 28.53 | 50.50 | 17.25 | 15.75 | 10.27 | | |
| (6) | Br | 56.8 | 213.3 | 52.1 | 64.1 | 37.5 | 29.2 | 51.0 | 17.9 | 16.7 | 10.4 | | |
| (7) | $CO_2H$ | 60.3 | 215.7 | 45.3 | 54.7 | 30.4 | 29.1 | 50.8 | 18.2 | 17.2 | 9.4 | 178.6 | |
| (8) | $CO{\cdot}NH_2$ | 60.3 | 215.8 | 45.6 | 55.4 | 30.7 | 29.2 | 50.4 | 18.3 | 17.3 | 9.6 | 174.8 | |
| (9) | $CO_2Me$ | 60.0 | 215.4 | 45.4 | 54.8 | 30.4 | 29.1 | 50.6 | 18.3 | 17.2 | 9.5 | 172.6 | 51.6 |
| (10) | COMe | 60.5 † | 215.7 | 45.4 | 60.9 † | 30.6 | 29.3 | 50.5 | 18.3 | 17.3 | 9.3 | 208.5 | 29.3 |
| (11) | $NO_2$ | 60.32 | 210.01 | 45.97 | 91.12 | 31.12 | 27.67 | 51.83 | 17.48 | 16.32 | 9.63 | | |
| (11a) | $NO_2$[3,3-$^2H_2$] | 60.33 | 210.05 | 45.34 | 90.97 | 31.02 | 27.67 | 51.79 | 17.48 | 16.28 | 9.63 | | |
| Norcamphor | | 49.86 | 217.95 | 45.25 | 35.35 | 27.23 | 24.21 | 37.70 | | | | | |
| [3-*exo*-$^2H_1$] | | 49.85 | 217.88 | 44.90 | 35.26 | 27.19 | 24.21 | 37.68 | | | | | |
| [3,3-$^2H_2$] | | 49.87 | 218.13 | 44.48 | 35.17 | 27.16 | 24.22 | 37.66 | | | | | |

† Reversible values.

TABLE 2

$^{13}$C Chemical shift increments of 4-substituted camphors

| Compd. | X | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) | C(9) | C(10) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| (1) | H | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| (2) | Me | 2.2 | 0.3 | 5.9 | 2.3 | 7.3 | −0.3 | 1.5 | −2.2 | −3.3 | 0.8 |
| (3) | $NH_2$ | 1.6 | −2.5 | 5.9 | 18.7 | 7.6 | −1.4 | 1.6 | −2.8 | −4.1 | 1.2 |
| (4) | OH | 1.1 | −2.7 | 5.0 | 36.5 | 6.2 | −2.0 | 1.5 | −2.7 | −4.0 | 0.8 |
| (5) | Cl | 0.5 | −5.6 | 7.7 | 26.9 | 9.3 | −1.3 | 4.0 | −2.4 | −3.3 | 1.1 |
| (6) | Br | −0.6 | −5.1 | 9.0 | 20.9 | 10.5 | −0.7 | 4.4 | −1.8 | −2.4 | 1.2 |
| (7) | $CO_2H$ | 2.9 | −2.7 | 2.2 | 11.5 | 3.4 | −0.8 | 4.2 | −1.5 | −1.9 | 0.2 |
| (8) | $CO{\cdot}NH_2$ | 2.9 | −2.6 | 2.5 | 12.2 | 3.7 | −0.7 | 3.8 | −1.4 | −1.8 | 0.4 |
| (9) | $CO_2Me$ | 2.6 | −3.0 | 2.3 | 11.6 | 3.4 | −0.8 | 4.0 | −1.4 | −1.9 | 0.3 |
| (10) | COMe | 3.1 | −2.7 | 2.3 | 17.7 | 3.6 | −0.6 | 3.9 | −1.4 | −1.8 | 0.1 |
| (11) | $NO_2$ | 2.9 | −8.0 | 2.9 | 48.7 | 4.1 | −2.2 | 5.2 | −2.2 | −2.8 | 0.4 |

The *syn*- [C(8)] is taken to absorb at lower field than the *anti*- [C(9)] methyl carbon nucleus for (1)—(11), in accord with precedent,[13] although, surprisingly for (1)—(11), γ-shifts for C(8) correlate only moderately (*r* 0.923) with those of C(9). These low field γ-shifts contrast, as with 4-substituted tricyclenes,[4] with high-field C(10) δ-shifts, although for the camphors (1)—(11) no meaningful correlation now exists between the C(10) and either the C(8) or the C(9) shifts.

The geometrical relationship between the C(4) substituent and the carbonyl group in the camphors (1)—(11) is such as to minimise any direct interaction. Here electron-withdrawing substituents cause shielding of the carbonyl carbon C(2) such that high-field γ-shifts show a reasonable empirical correlation (*r* 0.965) with the linear free energy parameter $\sigma_I$.[14] The generality of this empirical finding has yet to be established, although it is noted that shieldings of the $sp^2$-hybridised 2-carbon atoms in 1-substituted camphenes show a broadly similar substituent dependence.[5] The greater high-field γ-shifts observed for C(2) than for C(6) can be rationalised in terms of recent work [15] on linear electric field shifts, since unsaturated bonds possess appreciably greater polarisabilities than do saturated bonds, as a consequence of which the carbonyl carbon gives rise to greater electric field shift coefficients.

In the camphor series (1)—(11) the chemical shift differences are ascribed to differences within the paramagnetic shielding expression, $\sigma_p$ [equation (1)],[16] where

$$\sigma_p = -\frac{k}{\Delta E}\langle r^{-3}\rangle_{2p}[Q_{AA} + \sum_{A \neq B} Q_{AB}]$$

$\Delta E$ represents a mean excitation energy in the closure

---

[9] T. Pehk, M. Alla, and E. Lippmaa, *Org. Magnetic Resonance*, 1973, **5**, 351.

[10] E. Lippmaa, T. Pehk, and J. Paasivita, *Org. Magnetic Resonance*, 1973, **6**, 277.

[11] C. Altona and M. Sundaralingam, *J. Amer. Chem. Soc.*, 1970, **92**, 1995.

[12] R. L. Cargill, D. F. Bushby, P. D. Ellis, S. Wolff, and W. C. Agosta, *J. Org. Chem.*, 1974, **39**, 573.

[13] J. B. Stothers, C. T. Tan, and K. C. Teo, *Canad. J. Chem.*, 1973, **51**, 2893.

[14] O. Exner, in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 1.

[15] J. G. Batchelor, *J. Amer. Chem. Soc.*, 1975, **97**, 3410.

[16] J. A. Pople, *J. Chem. Phys.*, 1962, **37**, 53, 60; M. Karplus and J. A. Pople, *ibid.*, 1963, **38**, 2803.

approximation, $\langle r^{-3}\rangle_{2p}$ is the mean value of $r^{-3}$ where $r$ is the distance between the nucleus and the $2p$ electrons, $Q_{AB}$ represents a charge density term, and $Q_{AA}$ represents bond order terms.

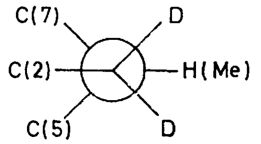
If the lowest energy transition is sufficiently lower in energy than other transitions it is possible to approximate the energy of this transition to $\Delta E$, and in the case of nitroso-compounds a correlation exists between $^{15}$N shifts, after diamagnetic correction, and the energy of the $n$–$\pi^*$ transitions.[17] An analogous identification of $\Delta E$ with the higher energy $n$–$\pi^*$ transition of ketones may not be so strictly in order; however this transition would contribute predominantly to $\Delta E$. Since $\lambda_{max.}$ and $\varepsilon$ are essentially the same for the representative examples (1), (4), (5), and (11) (see Experimental section) this transition does not, *via* $\Delta E$, account for C(2) shift dependence.

In addition we have prepared the 3,3-dideuterio-derivatives (2a), (5a), and (11a); their $^{13}$C spectra indicate, in accord with precedent, significant (0.6—0.9 p.p.m.) high-field shifts for the deuterium bearing carbon atoms, C(3), as compared with the respective protio-analogues (Table 1).[18] Similar though smaller isotope shifts are shown for $sp^3$-hybridised vicinal carbon atoms, C(4), whereas carbonyl carbon atoms, C(2), are generally deshielded. In the spectra of (2a), (5a), and (11a) the C(3) signal contains a quintet splitting $[{}^1J_{C(3)-D(3\text{-}exo)} = {}^1J_{C(3)-D(3\text{-}endo)}]$ of *ca.* 20.0 Hz.

In previous work, line broadening of the C(5) absorption, attributable to coupling with *exo*-deuterium, has been observed in the $^{13}$C n.m.r. spectrum of *inter alia* [3-*exo*-$^2H_1$]camphor, whereas in [3-*endo*-$^2H_1$]camphor only the C(7) absorption is broadened. Both these effects are due to the corresponding $^3J_{C-C-C-D}$ coupling, which exhibits the expected dihedral angle dependence.[13,19] In general $J_{C-C-C-H} > J_{C-C-H}$;[20] accordingly C(3) deuteriation in (2a), (5a), and (11a) causes no discernible change in the C(4) signal linewidth. In [3-*exo*-$^2H_1$]- and [3,3-$^2H_2$]-norcamphor, analogous line broadenings are noted for C(5), and C(5) and C(7), respectively. These effects are associated with modest isotope shifts for C(5) and C(7) which are $\gamma$ to deuterium (Table 1); previously small high-field shifts have been observed for carbons $\gamma$ to deuterium in freely rotating systems.[21] In the dideuterio-series (2a), (5a), and (11a) the C(5) $\gamma$ isotope shift is now definitely greater than that for the quaternary carbon C(7); this was apparent from both scale expanded spectra incorporating, in effect, more closely spaced data points and also the resolution of C(5) but not C(7) absorptions from solutions containing both all-protio- and dideuterio-camphors.

Additionally, it was hoped that in (2a) a vicinal coupling, $^3J_{C(11)-C(4)-C(3)-D(exo)}$, would assist in assignment of the exocyclic methyl carbon [C(11)] signal by means of line broadening of this absorption and/or a modest deuterium-induced isotope shift; however neither was observed. Assignment of the C(11) signal in (2) was possible with the aid of the deuteriomethyl compound (12),[22] where a high-field isotope shift of 0.30 p.p.m. was observed for C(11); additionally a smaller (0.08 p.p.m.) isotope shift was observed for C(4), whereas no deuterium-induced isotope shifts were found for C(3), C(5), and C(7), $\gamma$ to deuterium, nor were vicinal couplings observed between these carbon atoms and deuterium.

In the deuteriated norcamphors the essential absence of stereoselectivity in the very small deuterium-induced shifts for C(5) and C(7) provides no evidence for an explanation of these shifts based on an angular dependent inductive effect of deuterium.[23] As in [3,3-$^2H_2$]norcamphor the deuterium atoms in (2a), (5a), and (11a) are in an approximately antiperiplanar relationship with either C(5) or C(7) (see Figure), and in these camphors the greater deuterium-induced C(5) shift may be associated with the substituent patterns of these carbon atoms. It is of interest that in (2a) no deuterium-induced C(11) shift is observed; here the C(11)–C(4)–C(3)–D dihedral angles are both appreciably removed from the antiperiplanar situation (Figure). Recently it has been shown that high-field fluorine shifts brought about by vicinal deuteriation in norbornane and cyclohexane systems are greatest when the D(H)–C–C–F dihedral angle is greatest;[24] these results were interpreted in terms of an angular dependent inductive effect,[23] although such an explanation was not satisfactory for low dihedral angles.[24] The present results offer qualified support to this proposal; the upfield deuterium-induced shifts of $\gamma$-carbon atoms are consistent with hydrogen in a C–H bond being more electron-withdrawing than deuterium in a C–D bond[25] in relation to the general observation that electron-withdrawing substituents *exo* at C(2) in norbornane, where ' steric compression ' effects at C(6) are absent, bring about low-field shifts at C(6).[26]



FIGURE

We have also examined $^{13}$C chemical shifts of a series of 4-substituted *N*-nitrocamphorimines (13)—(17) (Table 3). For particular carbon atoms the response of

---

[17] J. Mason and W. van Bronswijk, *J. Chem. Soc. (A)*, 1970, 1763.

[18] (*a*) H. Batiz-Hernandez and R. A. Bernheim, *Progr. N.M.R. Spectroscopy*, 1967, **3**, 63; (*b*) H. N. Colli, V. Gold, and J. E. Pearson, *J.C.S. Chem. Comm.*, 1973, 408.

[19] J. B. Stothers, C. T. Tan, A. Nickon, F. Huang, R. Svidher, and R. Weglein, *J. Amer. Chem. Soc.*, 1972, **94**, 8581.

[20] J. B. Stothers, ' Carbon-13 NMR Spectroscopy,' Academic Press, New York, 1972.

[21] A. P. Tulloch and M. Mazurek, *J.C.S. Chem. Comm.*, 1973, 692.

[22] F. C. Brown, this Department, unpublished results.

[23] M. H. Pendlebury and L. Phillips, *Org. Magnetic Resonance*, 1972, **4**, 529.

[24] J. B. Lambert and L. G. Greifenstein, *J. Amer. Chem. Soc.*, 1974, **96**, 5120.

[25] M. Wolfsberg, *Accounts Chem. Res.*, 1972, **5**, 225.

[26] J. B. Grutzner, J. Jautelat, J. B. Dence, R. A. Smith, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, **92**, 7107.

chemical shift to substituent variation is very similar to that of the corresponding camphor.

Predictably, largest shielding differences between the camphor and its *N*-nitro-imine are observed for C(2), C(3), and C(1). Thus C(2) in the nitro-imines (13)—(17) is shielded by 27.3—30.2 p.p.m. with respect to C(2) in the parent camphor. Additionally we find that C(9) in *N*-nitrofluorenimine absorbs at 163.5 p.p.m., as compared with 193.4 p.p.m. in fluorenone and in the *N*-nitro-imine from pinacolone, C(3) absorbs at 181.4 p.p.m. whereas the corresponding absorption of pinacolone is at 210.7 p.p.m.[27] Previously it has been tentatively concluded that the imine bond in 4-substituted *N*-nitrocamphorimines is slightly less polar than the carbonyl bond in 4-substituted camphors on the basis of slightly smaller values of $^4J_{\mathrm{H(3\text{-}\mathit{exo})-H(5\text{-}\mathit{exo})}}$ obtained for *N*-nitro-imines.[28] The relative C(2) chemical shifts are consistent with but do not require this explanation;* however $^{13}C{=}N{-}NO_2$ shieldings are predictable within a few p.p.m. from a knowledge of the carbonyl shieldings.

TABLE 3

$^{13}C$ Chemical shifts (p.p.m. for $Me_4Si$) of 4-substituted *N*-nitrocamphorimines (13)—(17) and diazocamphors (18) and (19)

| Compd. | X | C(1) | C(2) | C(3) | C(4) | C(5) | C(6) | C(7) | C(8) | C(9) | C(10) | C(11) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| (13) | H | 53.4 | 189.4 | 35.2 | 43.5 | 26.8 | 31.7 | 48.9 | 19.4 | 18.7 | 10.4 | |
| (14) | Me | 55.8 | 188.7 | 40.8 | 46.3 | 33.9 | 31.3 | 50.0 | 17.0 | 15.0 | 11.1 | 16.0 |
| (15) | Cl | 53.3 | 184.5 | 42.8 | 70.0 | 35.8 | 30.6 | 52.1 | 16.8 | 15.8 | 11.5 | |
| (16) | $CO_2H$ | 56.7 † | 185.7 | 37.5 | 55.3 † | 30.3 * | 31.0 * | 53.0 | 17.9 | 17.1 | 10.6 | 178.0 |
| (17) | $NO_2$ | 55.8 | 183.2 | 38.2 | 91.4 | 31.0 * | 30.0 * | 53.6 | 17.2 | 16.4 | 10.8 | |
| (18) | H | 58.2 | 202.2 | 61.2 | 49.7 | 27.2 | 30.8 | 48.7 | 20.3 | 18.7 | 9.5 | |
| (19) | Me | 59.4 | 201.9 | 64.4 | 51.6 | 34.4 | 30.9 | 51.6 | 18.1 | 15.7 | 10.2 | 11.9 |

* Reversible values. † Reversible values

The nitro-imine group in (13)—(17) is capable of geometrical isomerism, although no evidence for this was found. Models indicate that a preferred configuration places the C(2)–C(3) bond *syn* to the N–N bond, whereas in the alternative configuration an oxygen of the nitro-group is situated close to the C(10) methyl group. In the latter situation steric compression may be expected to cause a significant shift of the C(10) signal with respect to the corresponding ketone. High-field steric compression shifts are considered to apply unambiguously only to $\gamma$-effects, and recently *syn*-axial $\delta$-interactions have been shown to result in low-field shifts in *trans*-decalol derivatives.[30] Since C(10) in compounds (13)—(17) is deshielded by only *ca.* 1 p.p.m. with respect to the corresponding ketone, it is probable that in this series a common configuration obtains in which C(2)–C(3) and N–N bonds are *syn*.

We have also determined $^{13}C$ and $^{15}N$ natural abundance spectra of some substituted diazoalkanes (Table 4). In compounds (18) and (19) C(2) is shielded by *ca.* 17 p.p.m. with respect to compounds (1) and (2), in accord with increased enolate character at this carbon atom. By contrast, C(3) in (18) and (19) is comparably deshielded with respect to (1) and (2), but still absorbs >100 p.p.m. to higher field than is normal for *sp*$^2$-hybridised carbon atoms bonded to nitrogen.[31] This high-field shift is presumably associated with a large electron density on C(3) which supports a significant contribution to the structure of the canonical form depicted in (18). Appreciable broadening of the C(3) absorption in proton noise-decoupled spectra of (18) and (19) is attributed to quadrupole broadening brought about by $^{14}N$. Smaller low-field methyl-induced $\beta$-shifts for C(3) with respect to C(5) in (19) reflect a general situation for *sp*$^2$- *vs.* *sp*$^3$-hybridised carbon atoms.

The $^{15}N$ chemical shifts of a number of diazoalkanes are given in Table 4. By means of (18) enriched with $^{15}N$ at the terminal nitrogen, N(2), it is shown that this nitrogen absorbs at 383 p.p.m., a value close to that (376 p.p.m.) for the corresponding nitrogen of diazomethane;[32] accordingly the low-field absorption in 9-diazofluorene is assigned to the terminal nitrogen.

TABLE 4

$^{13}C$ and $^{15}N$ chemical shifts (p.p.m.) of diazoalkanes and methyl azide

| | C [a] | Central N [b] | Terminal N [b] |
|---|---|---|---|
| Diazomethane | 23.1 | | 376 [d] |
| 3-Diazocamphor | 61.2 | 249 | 383 |
| 9-Diazofluorene | 75.2 | 266 | 420 |
| Methyl azide | | 226 [d] | 184 [e] |

[a] Solutions in $CDCl_3$; shifts of nitrogen-bonded carbon relative to internal $Me_4Si$. [b] Solutions in $CDCl_3$; shifts determined in the presence of 0.1M-Cr(acac)$_3$, relative to external $[NH_4]^+$. [c] Data from ref. 31. [d] Data from ref. 32. [e] Data from ref. 33 and converted relative to external $[NH_4]^+$.

Diazoalkanes are isoelectronic with alkyl azides; however the terminal nitrogen, N(2), in diazoalkanes is deshielded by *ca.* 230 p.p.m. with respect to its counterpart, N(3), in alkyl azides (actually determined as a $^{14}N$ shift),[33] whereas the central nitrogen, N(1), in diazoalkanes absorbs 23—40 p.p.m. downfield from the corresponding nitrogen, N(2), in alkyl azides. This relative chemical shift insensitivity of the central atom is broadly

---

* For a consideration of the relative chemical shifts of carbonyl and thiocarbonyl compounds see ref. 29.

[27] L. M. Jackman and D. P. Kelly, *J. Chem. Soc. (B)*, 1970, 102.

[28] D. G. Morris and A. M. Murray, *Org. Magnetic Resonance*, 1974, **6**, 510.

[29] H. Kalinowski and H. Kessler, *Angew. Chem. Internat. Edn.*, 1974, **13**, 90.

[30] S. H. Grover, J. P. Guthrie, J. B. Stothers, and C. T. Tan, *J. Magnetic Resonance*, 1973, **10**, 227; S. H. Grover and J. B. Stothers, *Canad. J. Chem.*, 1974, **52**, 870; T. Sato, T. Takemura, and M. Kainosho, *Tetrahedron Letters*, 1974, 97; J. Blunt, *Austral. J. Chem.*, 1975, **28**, 1017.

[31] J. Firl, W. Runge, and W. Hartman, *Angew. Chem. Internat. Edn.*, 1974, **13**, 270.

[32] L. F. Farnell, personal communication.

[33] M. Witanowski, *J. Amer. Chem. Soc.*, 1968, **90**, 5683.

shown by other molecules with a linear array of three 'heavy' atoms, as exemplified by the $^{13}C$ shifts of allene,[34] keten,[35] and nitrile oxides [36] and the nitrogen chemical shifts of the azide ion [33] and nitrous oxide.[37]

Nitrogen-15 chemical shift variations in a series of linear sixteen-valence-electron molecules gave a linear correlation with π-electron densities, with variations in the mean excitation energy, $\Delta E$, considered relatively unimportant.[37,38] With regard to terminal carbons, greater π-electron density has been proposed [34] in order to rationalise the shielding in keten with respect to allene, whereas the low-field shift in diazoalkanes with respect to keten is attributed [31] to reduction in σ-electron density on account of greater electronegativity of the $-N_2$ group. The results of current CNDO/2 calculations (Table 5) are consistent only with the second of these rationalisations.

TABLE 5

Excess charge densities in linear triatomic molecules, calculated in the CNDO approximation

| | Atom | $p_z$ | $p_y$ | Total π | σ | Total |
|---|---|---|---|---|---|---|
| Diazomethane | C | −0.485 6 | 0.046 6 | −0.439 0 | +0.181 3 | −0.257 7 |
| $CH_2$–N(1)–N(2) | N(1) | −0.233 3 | −0.008 3 | −0.241 6 | 0.550 1 | 0.308 5 |
| | N(2) | −0.506 1 | 0.216 7 | −0.289 4 | 0.148 7 | −0.140 7 |
| Allene | C(1) | −0.519 2 | 0 | −0.519 2 | +0.102 4 | −0.416 8 |
| $H_2C(1)=C(2)=CH_2$ | C(2) | 0.057 6 | 0.575 6 | 0.633 2 | −0.230 0 | 0.403 2 |
| Keten | C(1) | −0.321 6 | 0 | −0.321 6 | 0.051 7 | −0.269 9 |
| $H_2C(1)=C(2)=O$ | C(2) | 0.121 7 | 0.269 4 | 0.391 1 | −0.051 3 | 0.339 8 |
| | O | 0.515 7 | −0.360 6 | 0.155 1 | −0.373 2 | −0.218 1 |

Nitrogen-15 shifts for terminal nitrogens of molecules listed in Table 6 are found not to correlate linearly with π-electron density on these atoms; however these shifts do show reasonable correlation ($r$ 0.961) with the lowest energy transitions, although identification of these transitions with $\Delta E$ has been criticised.[33] For those compounds in Table 6 with lowest energy transitions corresponding to $\lambda_{max.}$ 300 ± 30 nm, a reasonable correlation exists between the $^{15}N$ shift of the terminal nitrogen atom and the π-electron density. These observations suggest that the shieldings of terminal nitrogens are influenced by both $\Delta E$ and π-electron density variations. For the central nitrogens no comparable correlations are, however, noted.

TABLE 6

$^{15}N$ ($^{14}N$) Chemical shifts of terminal nitrogen atoms and lowest energy transitions for diazoalkanes and related compounds

| | Chemical shift * | $\lambda_{max.}$/nm |
|---|---|---|
| 9-Diazofluorene | 420 [a] | 493 (MeOH) [a] |
| 3-Diazocamphor | 383 [a] | 403 (MeOH) [a] |
| Diazomethane | 376 [b] | 395 (hexane) [d] |
| Nitrous oxide | 284 [c] | 290 [e] |
| Methyl azide | 184.5 [c] | 287 (MeOH) [f] |
| Isocyanate ion | 66 [c] | 300 ($H_2O$) [g] |
| Isothiocyanate ion | 189 [c] | 300 ($H_2O$) [h] |
| Azide ion | 77 [c] | 225 ($H_2O$) [i] |

* Relative to external $[NH_4]^+$.

[a] This work. [b] Ref. 32. [c] M. Witanowski and G. A. Webb, *Ann. Reports N.M.R. Spectroscopy*, 1973, **5A**, 395. [d] R. Hoffmann, *Tetrahedron*, 1966, **22**, 359. [e] G. Herzberg, 'Electronic Structure of Polyatomic Molecules,' vol. 3, 1966, p. 505. [f] W. D. Closson and H. B. Gray, *J. Amer. Chem. Soc.*, 1963, **85**, 290. [g] J. W. Rabelais, J. R. McDonald, and S. P. McGlynn, *J. Chem. Phys.*, 1969, **51**, 5103. [h] J. R. McDonald, V. M. Scherr, and S. P. McGlynn, *J. Chem. Phys.*, 1969, **51**, 1723. [i] J. R. McDonald, J. W. Rabelais, and S. P. McGlynn, *J. Chem. Phys.*, 1970, **52**, 1332.

## EXPERIMENTAL

$^{13}C$ N.m.r. spectra were determined for *ca.* 0.4M-solutions in $CDCl_3$; the chemical shifts are quoted relative to internal tetramethylsilane as standard and refer to proton noise-decoupled spectra. A Varian XL 100 spectrometer (25.2 MHz), incorporating 1.25 Hz per data point, was employed for determination of $^{13}C$ n.m.r. spectra of (18) and (19); $^{13}C$ spectra of (2), (2a), (5), (5a), (11), and (11a) were recorded at 0.04 Hz per data point. The remaining $^{13}C$ spectra were recorded with a Bruker HFX 13 spectrometer (22.63 MHz) and are accurate to 0.1 p.p.m.; the same instrument was used for determination of $^{15}N$ chemical shifts (9.12 MHz), relative to external $[NH_4]^+$ with 2.5 Hz per data point. The Bruker spectra and the Varian spectra of (18) and (19) were recorded, respectively, at Queen Mary College, London, and the University of Edinburgh under the S.R.C. Fourier transform service. The remaining spectra were determined at the University of Glasgow.

M.p.s were recorded on a Kofler hot-stage apparatus, unless otherwise stated. Microanalytical determinations were carried out by the Microanalytical Department, University of Glasgow. I.r. spectra were determined with a Perkin-Elmer 227 spectrophotometer, and u.v. spectra with a Unicam SP 8000 spectrophotometer.

Several of the 4-substituted camphors were available by literature methods: (2);[39] (3), (4), (8);[40] (5);[41] (7);[42] (11).[4]

*4-Bromocamphor* (6).—Oxidation of 4-bromobornan-2-*exo*-ol [43] with Jones reagent in the manner previously described [4] gave *4-bromocamphor*, m.p. 194—195° (sealed capillary) [from light petroleum (b.p. 60—80°)] (Found: C, 52.05; H, 6.55. $C_{10}H_{15}BrO$ requires C, 51.95; H, 6.55%), $\nu_{max.}$ ($CCl_4$) 1 754 cm$^{-1}$.

*Methyl Camphor-4-carboxylate* (9).—A solution of the carboxylic acid (7) in ether was treated with diazomethane to give a sweet smelling *oil* which solidified (Found: C, 68.65; H, 8.5. $C_{12}H_{18}O_3$ requires C, 68.55; H, 8.65%), $\nu_{max.}$ 1 752 cm$^{-1}$.

---

[34] J. Firl and W. Runge, *Angew. Chem. Internat. Edn.*, 1973, **12**, 668.

[35] J. Firl and W. Runge, *Naturforsch.*, 1974, **29b**, 393.

[36] M. Christl, J. P. Warren, B. L. Hawkins, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1973, **95**, 4392.

[37] J. E. Kent and E. L. Wagner, *J. Chem. Phys.*, 1966, **44**, 3530.

[38] E. L. Wagner, *J. Chem. Phys.*, 1965, **43**, 2728.

[39] H. Toivonen, *Tetrahedron Letters*, 1968, 3041.

[40] J. Houben and E. Pfankuch, *Annalen*, 1931, **489**, 193.

[41] J. Houben and E. Pfankuch, *Annalen*, 1933, **501**, 219.

[42] S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. G. Morris, *J. Amer. Chem. Soc.*, 1972, **94**, 4615.

[43] F. Wasmmundt, K. B. Gilles, and J. A. Christiano, *Tetrahedron Letters*, 1969, 4311.

4-*Acetylcamphor* (10).[44]—To a solution of 2-*exo*-hydroxybornane-4-carboxylic acid (1.98 g, 10.0 mmol) in anhydrous tetrahydrofuran (50 ml) under dry nitrogen was added by injection through a serum cap a 2.1M-solution of methyllithium in hexane (Lithium Corporation of America; 14.5 ml, 30.5 mmol). After cautious addition of water (20 ml) and extraction with ether, the organic layer was shaken with saturated brine, dried ($MgSO_4$), filtered, and evaporated. The crude 4-acetylbornan-2-*exo*-ol (1.70 g) was oxidised with Jones reagent to give 4-acetylcamphor (1.52 g, 78%), m.p. 48° [from light petroleum (b.p. 60—80°)], $\nu_{max.}$ ($CCl_4$) 1 750, 1 719, and 1 698 $cm^{-1}$.

*Ultraviolet Spectra* (*in Methanol*).—Compound (1) showed $\lambda_{max.}$ 289 nm ($\varepsilon$ 32); compound (4) $\lambda_{max.}$ 285.5 nm ($\varepsilon$ 35); and compound (5) $\lambda_{max.}$ 288 nm ($\varepsilon$ 32). Compound (11) showed an apparent $\lambda_{max.}$ (MeOH) at 283 nm ($\varepsilon$ 81); this absorption probably contains contributions from both carbonyl and nitro-groups.

4-*Substituted* N-*Nitrocamphorimines*.—These were prepared by the method used by Brooks *et al.*[45] for preparation of *N*-nitrocamphorimine. 4-*Methyl*-N-*nitrocamphorimine* (14) had m.p. 61—62°, $\nu_{max.}$ (KBr) 1 645 m, 1 560s, and 1 310s $cm^{-1}$ (Found: C, 62.85; H, 8.55; N, 13.4. $C_{11}H_{18}N_2O_2$ requires C, 62.85; H, 8.65; N, 13.3%). 4-*Chloro*-N-*nitrocamphorimine* (15) had m.p. 84—85°, $\nu_{max.}$ (KBr) 1 649m, 1 570s, and 1 313s $cm^{-1}$ (Found: C, 52.15; H, 6.7; N, 12.4. $C_{10}H_{15}ClN_2O_2$ requires C, 52.2; H, 6.5; N, 12.4%). 2-*Nitroiminobornane*-4-*carboxylic acid* (16) had m.p. 184—185°, $\nu_{max.}$ (KBr) 1 647m, 1 568s, and 1 308s $cm^{-1}$ (Found: C, 55.0; H, 6.7; N, 11.65. $C_{10}H_{15}N_3O_4$ requires C, 55.15; H, 6.55; N, 11.6%). 4,N-*Dinitrocamphorimine* (17) had m.p. 144—145°, $\nu_{max.}$ (KBr) 1 650m, 1 578s, 1 537s, and 1 310s $cm^{-1}$ (Found: C, 50.05; H, 6.4; N, 17.25. $C_{10}H_{15}N_3O_4$ requires C, 49.8; H, 6.25; N, 17.4%).

*Diazocamphors*.—3-Diazocamphor (18) was prepared by the literature method.[46] 4-Methyl-3-diazocamphor (19) was obtained from (2) by the method of Wiberg *et al.*[47] 4-*Methylcamphorquinone* was prepared from (2) by the method of Evans *et al.*,[48] as yellow needles (from ethyl acetate–petrol), m.p. 125—127° (Found: C, 73.35; H, 9.0. $C_{11}H_{16}O_2$ requires C, 73.3; H, 8.95%). 4-Methylcamphorquinone mono-*p*-tolylsulphonylhydrazone was converted directly into (19), yellow *crystals* [from light petroleum (b.p. 60—80°)], m.p. 95° (Found: C, 69.0; H, 8.6; N, 14.75. $C_{11}H_{16}N_2O$ requires C, 68.7; H, 8.4; N, 14.5%).

3-[2-$^{15}N$]Diazocamphor was prepared by the method of Noyes *et al.*,[49] except that $^{15}N$-enriched sodium nitrite was used [obtained from 99.5% $^{15}N$-enriched sodium nitrite (Prochem Ltd.) and ' diluted ' to 10% $^{15}N$ enrichment for reaction with 3-aminocamphor].

*Deuteriated* 4-*Substituted Camphors*.—Sodium (0.13 g) was cautiously added in portions to [$^2H_4$]methanol (99%; Prochem Ltd.) (4 ml) with initial external cooling in ice. To the resulting solution were added the 4-substituted camphor [(2), (5), or (11) (5 mmol)], and $D_2O$ (1 ml), and this solution was set aside at room temperature for 4 weeks. After successive additions of pentane (20 ml) [for (11) a 1 : 2 pentane–ether mixture], glacial acetic acid (350 mg), and water (3 ml), the pentane layer was further extracted with water (3 × 2 ml). The pentane layer was then dried ($Na_2SO_4$), filtered, and evaporated. Mass spectral analysis showed for (2a) 0% $^2H_0$, 2% $^2H_1$, 98% $^2H_2$; for (5a) 0% $^2H_0$, 2% $^2H_1$, 98% $^2H_2$; for (11a), 0% $^2H_0$, 1.5% $^2H_1$, 98.5% $^2H_2$.

[3-*exo*-$^2H_1$]Norcamphor was prepared by the method of Jefford and Boschung.[50] Mass spectral analysis showed 3.0% $^2H_0$, 95.5% $^2H_1$, 1.5% $^2H_2$.

[3,3-$^2H_2$]Norcamphor was a gift from Professor K. H. Overton.

*N*-Nitrofluorenimine was prepared by the method of Horner *et al.*;[51] m.p. 140—141° (lit,[51] 141°). 3,3-Dimethyl-*N*-Nitrobutan-2-imine was prepared by the method of Suggitt *et al.*[52]

A. M. M. thanks the S.R.C. for support. We are grateful to Professors F. W. Wassmundt and K. H. Overton for samples of 4-bromobornan-2-*exo*-ol and [3,3-$^2H_2$]norcamphor, respectively, and to Miss E. W. Hughes, Dr. A. Boyd, and Dr. D. S. Rycroft for $^{13}C$ spectral determinations.

[6/302 *Received*, 12*th February*, 1976]

---

[44] M. Kagawa, *Chem. and Pharm. Bull.* (*Japan*), 1959, **7**, 306.

[45] S. G. Brooks, R. M. Evans, G. F. H. Green, J. S. Hunt, A. G. Long, B. Mooney, and L. J. Wayman, *J. Chem. Soc.*, 1958, 4614.

[46] J. Bredt and W. Holz, *J. prakt. Chem.*, 1917, **95**, 133.

[47] K. B. Wiberg, B. R. Lowry, and T. H. Colby, *J. Amer. Chem. Soc.*, 1961, **83**, 3998.

[48] W. C. Evans, J. L. Simonsen, and W. V. Bhagvat, *J. Chem. Soc.*, 1934, 444.

[49] W. A. Noyes and E. Meitzner, *J. Amer. Chem. Soc.*, 1932, **54**, 3768.

[50] C. W. Jefford and A. F. Boschung, *Helv. Chim. Acta*, 1974, **57**, 2242.

[51] L. Horner, L. Hockenberger, and W. Kirmse, *Chem. Ber.*, 1961, **94**, 290.

[52] J. W. Suggitt, G. S. Myers, and G. F. Wright, *J. Org. Chem.*, 1947, **12**, 373.