Conformations of Cyclic and Acyclic Cyanides: ^{13}C–H Couplings

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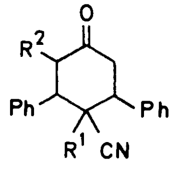
Natural abundance ^{13}C n.m.r. spectra were determined for molecules such as methyl 1-cyano-4-oxo-2,6-diphenylcyclohexanecarboxylate and 4-oxo-1,2,6-triphenylcyclohexanecarbonitrile. The use of three-bond couplings between cyanide and hydrogen proved to be a useful tool in the assignment of configuration of cyclic molecules. In certain rigid molecules *trans*-^{13}CN and H groups are characterized by a coupling of 9 Hz, whereas *gauche*-nuclei have a coupling of 2 Hz. In conformationally mobile systems, the use of ^{1}H vicinal couplings in conjunction with the ^{13}C couplings provides strong evidence for preferred conformation. In certain highly substituted cyclohexanones, the importance of non-chair (probably twist-boat) conformers is evident.

THE purpose of this work was to investigate couplings between cyanide and hydrogen with the intention of using these as a probe for conformation and configuration. Marshall *et al.* have reviewed the as yet limited data on ^{13}C–H as well as on ^{13}C–^{13}C couplings in a variety of molecules.[1] Goldstein *et al.* have also reviewed ^{13}C couplings in aromatic structures.[2] A recent article by Wilson and Stothers on the stereochemical applications of ^{13}C n.m.r. emphasized the use of chemical shifts but not of coupling constants.[3]



(1), (2) R^1=CO$_2$Me, R^2=H
(3), (4) R^1=Ph, R^2=H
(5) R^1=Ph, R^2=CO$_2$Me
(6) R^1=CN, R^2=H

TABLE 1

^{1}H Chemical shifts and coupling constants

Compound [b]	J/Hz $^3J_{2a,3a}$	$^3J_{2a,3e}$	$^2J_{3a,3e}$	$^2J_{5,5'}$	$^3J_{5,6}$	$^3J_{5',6}$	δ H-2a	H-3a	H-3e	H-5	H-5′	H-6	R^1
(1)	14.5	3.5	−14.9	*a*	*a*	*a*	3.74	3.29	2.74	*a*	*a*	*a*	3.26(CH$_3$)
(2)	13.5	3.7	−16.9	−16.8	~7.7	~5.3	3.97	3.17	2.81	3.18	3.04	3.98	3.38
(3)	14.2	3.3	−14.7	*a*	*a*	*a*	3.72	3.51	2.82	*a*	*a*	*a*	
(4)	13.7	4.4	−16.0	−16.6	7.1	2.2	3.92	3.35	2.95	3.54	2.94	3.78	
(5) [d]	14.2	3.6	−14.7			13.3	3.84	3.69	2.93		4.13	4.58	
(6)	6.9 [c]	6.9 [c]		*a*	*a*	*a*	3.82	3.07	3.07	*a*	*a*	*a*	

[a] Because of the symmetry of the molecule, this value is the same as the previous entry. [b] Sample concentration; 5% (w/v) in CDCl$_3$. Me$_4$Si was the standard. [c] Line separations are given; the spectra are ' deceptively simple.' [d] 5-Methyl ester absorption at δ 3.54.

Perlin and Lemieux and their co-workers have suggested that a Karplus relationship exists between $^3J_{CH}$ and the dihedral angle.[4] Thus, *trans*-nuclei are characterized by $^3J_{CH}$ values of 6—9 Hz, whereas *gauche*-nuclei show $^3J_{CH}$ values of 0—2 Hz. However, Feeney *et al.* have suggested that $^3J_{CH}$ values of *ca.* 12 and 0.4 Hz pertain where the carbon nucleus is part of a carbonyl group.[5,6] sp^1 Hybridized carbon nuclei have not been studied in detail. In older work, Karabatsos suggested that progressively larger coupling constants occur with increasing *s* character: sp^3 (0.3), sp^2 (0.4), sp^1 (0.6), where the numbers in parentheses refer to the magnitude of $^3J_{CH}$ relative to $^3J_{HH}$.[7] Later, Karabatsos and Lemieux warned of substantial variations in $^3J_{CH}$ due to stereoelectronic factors.[4,8]

In order to establish limiting values for $^3J_{CH}$ for cyanide, it was necessary to study certain rigid molecules. Suitable compounds (1)—(6) were available from earlier

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[1] J. L. Marshall, D. Miller, S. Conn, R. Seiwell, and A. Ihrig, *Accounts Chem. Res.*, 1974, **7**, 333, and references therein.

[2] J. H. Goldstein, V. Watts, and L. Rattet, *Progr. N.M.R. Spectroscopy*, 1972, **8**, 104.

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

[4] (*a*) J. Schwartz and A. Perlin, *Canad. J. Chem.*, 1972, **50**, 3667; (*b*) L. T. J. Delbaere, M. James, and R. U. Lemieux, *J. Amer. Chem. Soc.*, 1973, **95**, 7886; (*c*) see however R. U. Lemieux and J. Koto, *Tetrahedron*, 1974, **30**, 1933.

[5] J. Feeney, P. Hansen, and G. Roberts, *J.C.S. Chem. Comm.*, 1974, 465.

[6] M. Rennekamp and C. Kingsbury, *J. Org. Chem.*, 1973, **38**, 3959.

[7] G. J. Karabatsos, J. D. Graham, and F. Vane, *J. Phys. Chem.*, 1961, **65**, 1657.

[8] G. J. Karabatsos and C. E. Orzech, jun., *J. Amer. Chem. Soc.*, 1964, **86**, 3574.

work.[9-11] The ^{1}H spectra of the cyano-esters (1) and (2) were recently reported by Otto.[12] Our ^{1}H data are recorded in Table 1 and the ^{13}C data are given in Table 2.

Compounds (1), (3), and (5) (Scheme 1) are nearly conformationally pure; each has a preponderance of equatorial groups. In the ^{1}H spectrum, $^3J_{2a,3a}$ (*ca.* 14.2 Hz) is larger than the coupling constant for diaxial protons in cyclohexane.[13,14] The coupling constants suggest that the ring is less flattened than simple cyclohexane derivatives.[15] In (1) and (3), application of the angle determination method of Garbisch and Griffith yields an average dihedral angle in the vicinity of 60°.[13] Ring flattening would increase the presumably repulsive interactions between the equatorial-axial-equatorial groups at C-6, -1, and -2.[16]

TABLE 2

^{13}C Chemical shifts and coupling constants

Compound	*J*/Hz		Chemical shift (p.p.m.)							
	$^3J_{CN,2a}$	$^3J_{CN,6}$	CN	C-1	C-2	C-3	C-4	C-5	C-6	R^1
(1)	9.5	9.5	115.6	59.4	52.9	48.5	204.3	*a*	*a*	166.3 [c] 43.4 [d]
(2)	9.0	4.3	118.0	55.5	53.0	48.0	206.5	42.8	41.5	166.7 [c] 42.3 [d]
(3)	8.5	8.5	118.8	56.7	52.2	45.6	205.7	*a*	*a*	
(4)	9.0	4.3	122.1	52.2	53.3	47.4	207.3	44.2	42.3	
(5) [b]	9.3	9.3	118.6	61.0	52.1	45.2	201.1	60.2	54.0	
(6)	6.0 or 2.8	6.0 or 2.8	113.5	44.7	45.4	42.1	204.1	*a*	*a*	113.5 [e]

[a] Because of the symmetry of the molecule, this value is the same as the previous entry. [b] 5-Methyl ester absorption at 51.4 p.p.m. [c] Carbonyl. [d] Methyl ester. [e] Cyanide.

The ^{13}C coupling constants involving cyanide ($^3J_{CN,2a}$ and $^3J_{CN,6a}$ *ca.* 9 Hz) are in agreement with other results from our laboratory in suggesting a *trans*-orientation of these nuclei.[17] Thus, in (1), (3), and (5), cyanide is axial.

In (1) and (3), H-3e lies over the face of the 2-phenyl group. This shielding influence is augmented by the shielding effect of carbonyl,[18] whose bond axis virtually parallels H-3e. Since H-3a lies over the centre of the axial CN triple bond, deshielding effect is expected.[19,20] The combination of these effects produces a rather large difference in chemical shift for H-3e [δ 2.74 in (1)] and H-3a (δ 3.29).

Compounds (2) and (4) are isomeric with (1) and (3) respectively. The spectra show that a change occurred in orientation of the 6-phenyl group rather than the seemingly easier interchange of groups at C-1. In (2) and (4), $^3J_{2a,3a}$ (*ca.* 13 Hz) and $^3J_{2a,3e}$ (*ca.* 4 Hz) are roughly the same as in (1) and (3), and these ^3J values are indicative of a high degree of conformational purity. However, in (4), $^3J_{5,6}$ (*ca.* 7 Hz) and $^3J_{5',6}$ (*ca.* 2 Hz) are suggestive of considerable conformational averaging. It seems likely that a non-chair conformation is partially occupied in (2) and (4). One possibility is the ' flexible ' conformation (4b) (Scheme 1).[21] In the equilibrium between the flexible and chair conformers, H-2a, -3a, and -3e evidently maintain a relatively constant orientation. The motion in these molecules evidently involves C-5 and -6 and attached groups.[22] In cyclohexanone, the flexible form is *ca.* 3 kcal mol^{-1} less stable than the chair form.[21] In (2) and (4), the difference in energy between the two conformers should be less since the axial phenyl group in the chair form is able to assume a more stable orientation in the flexible form.

With regard to carbon coupling constants, $^3J_{CN,H\text{-}2a}$ is assigned the 9 Hz value, and $^3J_{CH,H\text{-}6}$ is assigned the 4.3 Hz value. The latter is considerably larger than the limiting value of *ca.* 2 Hz for *gauche*-nuclei, and this coupling constant also is suggestive of conformational mixing.*

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* In *erythro*-2,3-dicyano-4-methylpentane, which as 92% *trans*-CN groups, $^3J_{CN,H}$ is 3 Hz.[17] In propiononitrile and in methyl cyanopropionate, the ' averaged ' coupling constant, $^3J_{CN,H}$, involving methyl is *ca.* 6 Hz.

[9] E. P. Kohler and R. Helmkamp, *J. Amer. Chem. Soc.*, 1924, **46**, 1018.

[10] S. Avery, *J. Amer. Chem. Soc.*, 1928, **50**, 2512.

[11] R. Helmkamp, L. Tanghe, and J. Plati, *J. Amer. Chem. Soc.*, 1940, **62**, 3215.

[12] H. Otto, *Arch. Pharm.*, 1972, **305**, 913; our assignment for CN (axial) is in disagreement with Otto's assignment for (1).

[13] E. Garbisch, jun., and M. Griffith, *J. Amer. Chem. Soc.*, 1968, **90**, 6543.

[14] G. Pouzard, M. Rajzmann, H. Bodot, and L. Pujol, *Org. Magnetic Resonance*, 1973, **5**, 209.

[15] F. A. L. Anet, *J. Amer. Chem. Soc.*, 1962, **84**, 1053.

[16] J. Lambert, *Accounts Chem. Res.*, 1971, **4**, 87.

[17] C.-H. Wang and C. Kingsbury, *J. Org. Chem.*, 1975, **40**, 3811.

[18] G. J. Karabatsos, G. Sonnichsen, N. Hsi, and D. Fenoglio, *J. Amer. Chem. Soc.*, 1967, **89**, 5067.

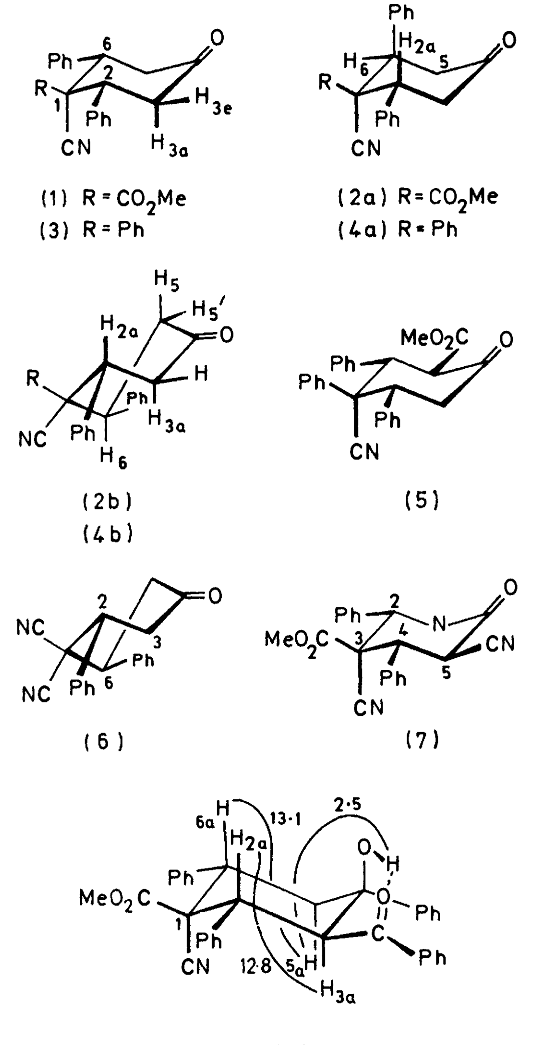
[19] J. A. Elvidge, ' Nuclear Magnetic Resonance for Organic Chemists,' ed. D. W. Mathieson, Academic Press, London, 1967, p. 33.

[20] (*a*) G. S. Reddy, J. H. Goldstein, and L. Mandell, *J. Amer. Chem. Soc.*, 1961, **83**, 1300; (*b*) S. Balasubrahmanyam and M. Balasubramanian, *J. Chem. Soc.* (*B*), 1970, 212.

[21] (*a*) A. Meyer, J. Schlesinger, and E. Bergman, *J. Chim. Phys. Physiochim. Biol.*, 1971, **68**, 674; (*b*) R. D. Stolow, M. Gattuso, N. Hefinger, R. Shone, and W. White, *Tetrahedron Letters*, 1971, 219; (*c*) B. Rickborn, *J. Amer. Chem. Soc.*, 1962, **84**, 2414; (*d*) N. L. Allinger, H. Blatter, L. Freiberg, and F. Karkowski, *ibid.*, 1966, **88**, 2999, and earlier papers; (*e*) M. Bernard, L. Canuel, and M. St. Jacques, *ibid.*, 1974, **96**, 2929; (*g*) K. Pihlaja, *J.C.S. Perkin II*, 1974, 890; (*h*) M. Gasić, Z. Djarmati, and S. W. Pelletier, *J. Org. Chem.*, 1976, **41**, 1219; (*i*) M. Hanack, and K: Heinz, *Annalen*, 1965, **682**, 75.

[22] (*a*) W. G. Bentrude and H. Tan, *J. Amer. Chem. Soc.*, 1974, **45**, 4666; (*b*) G. M. Kellie and F. G. Riddell, *Topics Stereochem.*, 1974, **8**, 225.

The geminal coupling constants, ${}^2J_{3a,3e}$ also indicate the presence of other conformations in (2) and (4).

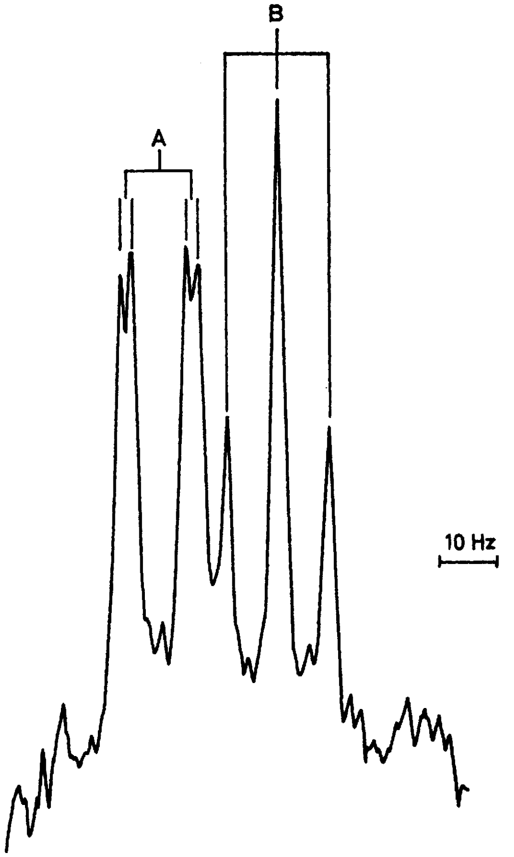


Scheme 1

According to Barfield and Grant, the orientation of carbonyl affects the ${}^2J$ value of the neighbouring methylene hydrogens.[23] In (1) and (3), H-3e lies near the node of the carbonyl π bond, and the effect of CO on ${}^2J$ is small (${}^2J_{3a,3e}$ −14.5 Hz).[24,25] In the flexible form, however, Dreiding models suggest that a variety of orientations of CO with respect to CH$_2$ is possible. The optimum conformation for the CO effect on ${}^2J$ (where the CO bond bisects the H–C–H angle), and another favourable conformation (where the H-3a bond parallels the CO p orbitals) are probably substantially populated. In (2) and (4), ${}^2J_{3a,3e}$ decreases to −16.5 Hz; ${}^2J_{5,5'}$ is similar.

In (2a) and (4a), the axial 6-phenyl group should shield H-2a, but in fact H-2a is deshielded [δ 3.92 in (4)] compared with H-2a in (3) (δ 3.7), consistent with the importance of other conformers such as (2b) or (4b). In (2) and (4) the difference in ${}^3J_{5,6}$ and ${}^3J_{5',6}$ and the difference in chemical shift for H-5 and -5′ suggest that rather different conformers are populated, but it is not possible to define the differences at present. The extreme deshielding of H-5 in (4) and its fairly large coupling constant to H-6 leads to the assignment of H-5 and -5′ as indicated in structure (4b).

The dicyanide (6) represents an interesting, but not easily explained case. H-3a and -3e have equivalent chemical shifts. The ^{1}H spectrum shows only a doublet for H-3 and a triplet for H-2. No stereochemical information can be derived from this deceptively simple spectrum.[26] The ^{13}C spectrum of cyanide shows equivalent CN chemical shifts, but each CN has non-equivalent coupling constants to H-2 and -6 (6.0 and 2.8 Hz or *vice versa*). The flexible form shown in Scheme 1 could account for the data. A pair of interconverting chair forms would probably give rise to equivalent coupling constants for either CN to H-2 and



^{13}C Spectrum of (7) (cyanide region only): A, 5-CN; B, 3-CN

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[23] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

[24] C. Kingsbury, R. Egan, and T. Perun, *J. Org. Chem.*, 1970, **35**, 2913.

[25] A. A. Bothner-By, *Adv. Magnetic Resonance*, 1965, **1**, 115.

[26] R. J. Abraham and H. J. Bernstein, *Canad. J. Chem.*, 1961, **39**, 216.

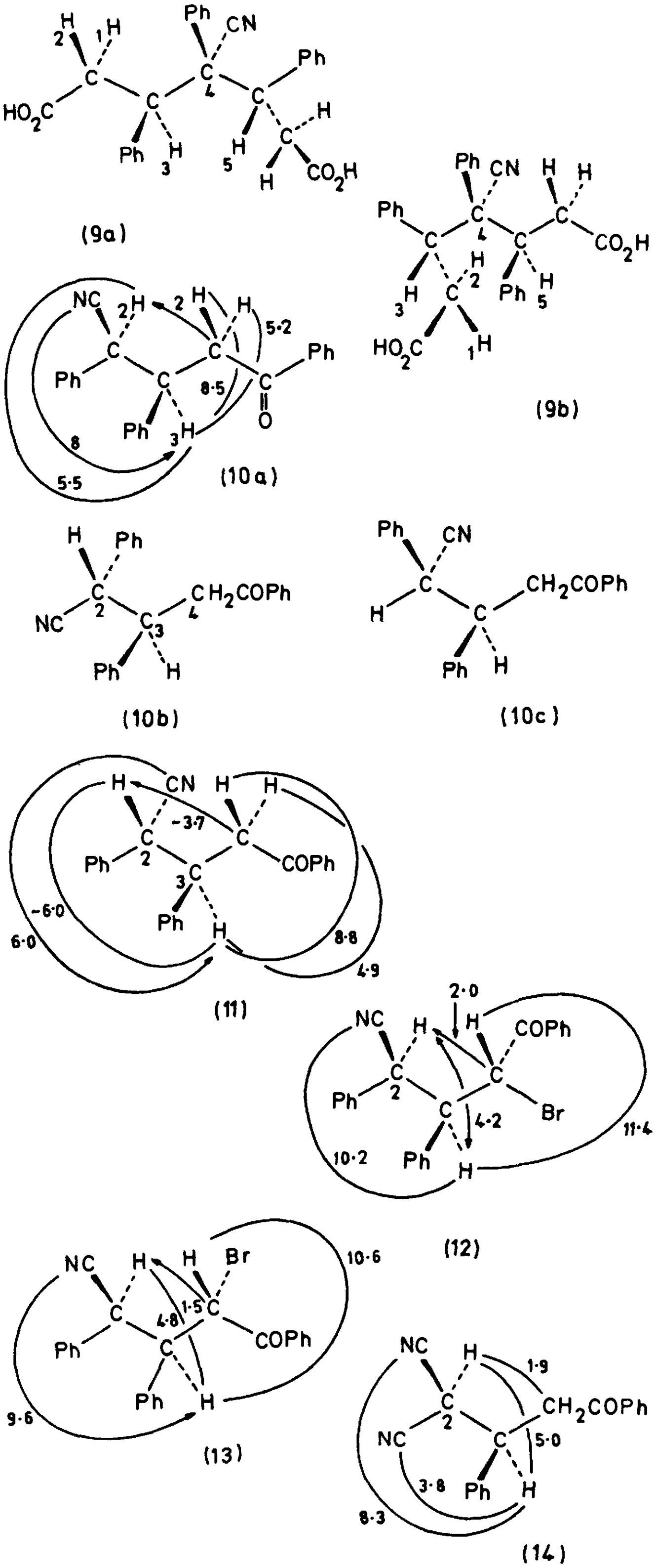
-6. An admixture of the chair forms with the flexible form (6) is possible, however.

In the case of compound (7), the recently established piperidone structure[27] supersedes the cyclobutane structure favoured by early workers,[28] but the configuration at C-3 was not firmly established. Two cyanide resonances evident in the ^{13}C n.m.r. spectrum (Figure). The 3-cyano-group showed a triplet pattern with $^{3}J_{\text{CN-H}}$ 8.8 Hz. Similar to (1), (3), and (5) this CN is axial. The 5-cyano-group showed coupling constants of 11.4 and 2.1 Hz. Two-bond couplings to CN are very large,[17] and thus $^{3}J_{\text{CN},4a}$ is the 2.1 Hz value which should be representative of *gauche*-nuclei. The equatorial orientation of this CN is in agreement with the large $^{3}J_{4a,5a}$ (13.2 Hz).

The final cyclic compound of interest, (8), resulted from condensation of methyl cyanoacetate with two equivalents of chalcone. The revised structure is cyclic,[29] and not open chain as indicated in the original paper,[30] but configuration remains unknown. Similar to (1) and (3), the largest ring substituents are equatorial, as indicated by the ^{1}H coupling constants shown in Scheme 1. The $^{3}J_{\text{CN,H}}$ value (9.6 Hz) proves that CN is again axial. The equatorial methoxycarbonyl group was coupled to H-2a and -6a by a small value (<2 Hz), similar to (1), but esters are one of the hardest groups to study due to weak intensity and extensive splitting, and these values remain tentative. The hydroxy-group appears as a doublet due to hydrogen bonding to the benzoyl group, which slows OH exchange and holds OH in a specific geometry.[24,31] The hydroxy-group is coupled to H-5a ($^{4}J_{\text{OH},5a}$ 2.5 Hz) through the well known W pathway. This splitting is eliminated by D_2O.

Acyclic Cyanides.—It was of interest to study open chain molecules embodying certain structural features of the cyclic compounds discussed above. In (9), the ^{1}H coupling constants indicate a considerable degree of conformational purity at C-2 and -3, which are equivalent to C-6 and -5 respectively ($^{3}J_{1,3}$ 2.7, $^{3}J_{2,3}$ 11.2 Hz). The equivalence of H-3 and -5 proves that (9) is one of the *meso*-isomers, since a (±)-structure would have non-equivalent protons.[25,32] The configuration at C-4 remains tentative, but it probably is as indicated in Scheme 2 as H-2 (δ 2.7) is shielded by the 4-phenyl group in certain conformations, and H-1 (δ 3.3) is deshielded by cyanide or by the 5-Ph group.

The i.r. spectrum in CH_2Cl_2 solution (0.5 mg ml^{-1}) showed an intense monomeric carboxy-absorption at 1 752 cm^{-1} compared to the dimeric carboxy-absorption



Scheme 2

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[27] (*a*) H. Böhme and S. Ebel, *Chem. Ber.*, 1965, **98**, 1819; (*b*) G. Dietz, W. Fiedler, and G. Faust, *ibid.*, 1967, **100**, 3127.

[28] (*a*) J. T. Carrick, *J. prakt. Chem.*, 1892, [2]**45**, 500; (*b*) C. Bertini, *Gazzetta*, 1901, **31I**, 272.

[29] C. Allen, T. Davis, W. Humphlett, and D. Stewart, *J. Org. Chem.*, 1957, **22**, 1291.

[30] E. P. Kohler, A. Graustein, and D. Merrill, *J. Amer. Chem. Soc.*, 1922, **44**, 2536.

[31] J. C. Jochims and G. Taigel, *Tetrahedron Letters*, 1968, 5483; see also ref. 24.

[32] K. Mislow and M. Raban, *Topics Stereochem.*, 1967, **1**, 1. For a different type of interpretation see R. P. Clifford and D. Ewing, *Org. Magnetic Resonance*, 1972, **4**, 473. See also F. A. Bovey, 'Polymer Conformation and Configuration,' Academic Press, New York, 1969, pp. 73—90.

at 1 730 cm^{-1}.[33] The latter tended to disappear at lower concentration. Thus, the carboxy-groups are not intramolecularly associated.

The ^{13}C spectrum of CO_2^- (pD *ca.* 9 in D_2O) showed a doublet of triplets with line separations of *ca.* 5 (triplet) and *ca.* 2 Hz (doublet). Because of the magnitudes of separations of the ^1H resonances, the 2 Hz value is very close to the true coupling constant. Thus, CO_2^- and H-3 are predominately *gauche.* In contrast, the spectrum of cyanide showed an 'average' coupling constant ($^3J_{CN,H-3}$ *ca.* 6 Hz), which suggests that (9) and its mirror image are the most likely contributing conformers. Thus, in (9a), CN is *gauche* to H-3 and *trans* to H-5, but in the mirror image CN is *trans* to H-3 and *gauche* to H-5. The resulting ^3J value is roughly the average of the limiting 9 and 2 Hz values for *trans-* and *gauche*-nuclei. This molecule is an interesting example in that conformational integrity is maintained at C-2 and -3, whereas conformational mixing occurs at the more sterically hindered carbons C-3, -4, and -5.

Other compounds of interest include the cyanides (10) and (11), whose relative configuration was previously unknown. The ^1H spectrum of the low melting isomer (11) was easily solved, but the spectrum of (10) was clarified only by using a 300 MHz instrument. The coupling constants, as reproduced by computer simulation, are shown in Scheme 2. For (10), the combination of the coupling constants for various sets of nuclei ($^3J_{CN,H-3}$ *ca.* 8, $^3J_{H-2,H-3}$ 5.4, and $^3J_{C-4,H-2}$ *ca.* 2 Hz) permits a rough estimation the weights of conformers (10a—c) as 0.7, 0.2, and 0.1 $\pm$ 0.1.[34] In the case of (11), a somewhat greater conformational purity is present with respect to C-3 and -4, but the molecule is highly mixed with respect to C-2 and -3. Using coupling constants for various sets of nuclei as before, the conformer shown in Scheme 2 is estimated to have a slightly greater weight (0.45) than the two other conformers resulting from rotation about C-2 and -3 (roughly 0.3 each).

Compounds (12) and (13) result from bromination of either (10) or (11). The ^1H spectra indicate that bromine has attacked C-4 and not C-2 as originally suggested by Kohler *et al.*[35] The orientation of groups at C-2 resembles that in (10), with the distinction that a greater conformational purity is present [conformational weight $\geqslant$0.9 for (12)].*

The dicyanide (14) shows a surprising degree of conformational purity despite the small size of the cyanides, which should permit a variety of conformations to be present at C-2. Thus, the conformation shown for (14) comprises roughly 0.7 of the total. The orientation of the C-4 protons is not determinable because of chemical shift equivalence.[26]

The acyclic cyanides (10) and (12)—(14) exhibit a remarkable tendency to have cyanide *gauche* to the 3-phenyl group. In the case of (14) the 3-phenyl group is *gauche* to both cyanides, although a seemingly less sterically hindered conformation results if one cyanide assumes a *trans*-orientation with respect to phenyl. In (11), the conformers with CN *gauche* to 3-Ph place 2-Ph in a rather unfavourable position, yet these conformers are substantially populated (combined weight *ca.* 0.6). Several possibilities exist to explain the conformational preference for *gauche* CN–Ph groups: (i) an attractive polarizability interaction between CN and Ph,[36] (ii) the hyperconjugation postulate of Pople *et al.*[37] and of Hoffman,[38] whereby electronegative groups (*e.g.* CN) prefer a *trans*-orientation with respect to hydrogen,[39] and (iii) geminal bond angle variations, such as used by Allinger *et al.* to explain the preference for *gauche* hydrogens in 2,3-dimethylbutane or 1,1,2,2-tetrabromoethane.[40]

In conclusion, the predicted order of $^3J_{CH}$ values: $sp^3 < sp^2 < sp^1$ does not appear to be upheld in the case of the sp^1 hybridized cyanides of this study, which have smaller J_T values than carbonyl. However, judgement should be withheld pending the acquisition of more extensive data.

EXPERIMENTAL

Preparation of Methyl 1-*Cyano*-4-*oxo*-2,6-*diphenylcyclohexanecarboxylates* (1) *and* (2).—These materials were prepared by the method of Kohler and Helmkamp: (1) (58% yield), m.p. 149—151° (lit.,[9] 148—149°); (2) (60% yield), m.p. 139—140° (lit.,[9] 137—138°).

Preparation of 4-*Oxo*-1,2,6-*triphenylcyclohexanecarbonitriles* (3) *and* (4).—The lower melting isomer was prepared by condensation of benzyl cyanide and dibenzalacetone by the method of Helmkamp *et al.*: (4) (40% yield), m.p. 190—192° (lit.,[11] 191°). The high melting isomer was prepared by isomerization of the low melting isomer with hydroiodic acid: (3) (62% yield), m.p. 210—211° (lit.,[11] 213°).

Preparation of Methyl 3-*Cyano*-6-*oxo*-2,3,4-*triphenylcyclohexanecarboxylate* (5).—This compound was prepared by the method of Avery: (5) (52% yield), m.p. 238—242° (lit.,[10] 242—244°). Although the m.p. was quite broad, the n.m.r. spectrum showed no sizeable impurity.

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* The configuration at C-4 is tentative for (12) and (13). The decision rests on the shielded nature of H-2 in (12) relative to (13) [H-2 lies over the face of CO in (12)]. On treatment with base, (12) was converted into a cyclopropane derivative, m.p. 168°, with $^3J_{HH}$ 7 Hz (*trans*-protons). Treatment of (13) with base gave a cyclopropane derivative, m.p. 172°, with equivalent protons, which could not be separated with shift reagents.

[33] R. T. Conley, 'Infrared Spectroscopy,' Allyn and Bacon, Boston, 1972, p. 161.

[34] Limiting values for ^1H coupling constants of 13 and 3 (ref. 14), and for ^{13}CO and ^1H of 13 and 2 Hz (ref. 6) were used. See also N. Sheppard and J. Turner, *Proc. Roy. Soc.*, 1959, *A*, **252**, 506.

[35] E. P. Kohler and C. Allen, *J. Amer. Chem. Soc.*, 1924, **46**, 1522.

[36] C. Kingsbury, *J. Org. Chem.*, 1968, **33**, 1128.

[37] L. Radom, W. Lathan, W. Hehre, and J. Pople, *J. Amer. Chem. Soc.*, 1973, **95**, 693.

[38] R. Hoffman, L. Radom, J. Pople, P. Schleyer, W. Hehre, and L. Salem, *J. Amer. Chem. Soc.*, 1972, **94**, 6221.

[39] M. J. S. Dewar, in 'Hyperconjugation,' Ronald Press, New York, 1962, has inveighed against hyperconjugation as a determining factor in the ground state properties of molecules. Ingold and Griller, *Accounts Chem. Res.*, 1976, **9**, 13, discount hyperconjugation as a factor in the conformation of free radicals.

[40] N. L. Allinger, J. Hirsch, M. Miller, I. Tyminski, and F. Van Catledge, *J. Amer. Chem. Soc.*, 1968, **90**, 1199.

Preparation of 4,4-*Dicyano*-3,5-*diphenylcyclohexanone* (6).—This compound was prepared by the general method of Tanaka and Imota.[41] In our procedure, malononitrile (1 g, 0.015 mol) and dibenzalacetone (3.5 g, 0.015 mol) was allowed to stand overnight in 95% ethanol (10 g) to which sodium hydride (*ca.* 0.1 g) had been added. Acetic acid was added to apparent neutrality, and the reaction mixture was poured into water. A precipitate formed which was filtered off giving crude product (1.3 g, 29%). This material was taken up in CH_2Cl_2, dried ($MgSO_4$), filtered, ethanol added, and the solvent was partially evaporated on a steam-bath. On cooling, crystals formed which were recrystallized from CH_2Cl_2–ethanol, m.p. 174.5—175.5° (lit.,[41] 174—175°). In other runs, the reaction mixture was refluxed for 24 h in an attempt to obtain the other isomer. A material precipitated from the dark red reaction mixture upon cooling, m.p. 240°, but this material was intractable.

Preparation of Ethyl 3,5-*Dicyano*-2,4-*diphenyl*-6-*oxopiperidine*-3-*carboxylate* (7).—This compound was prepared by the method of Carrick (51% yield plus some less pure fractions of the same material), m.p. 204—205° (lit.,[28] 204°), δ ($CDCl_3$) 0.84 (3 H, t, *J* 7.1 Hz, CH_3CH_2O), 3.72 (1 H, q, *J* 7.1 Hz, CH_3CH_2O), 3.73 (1 H, q, *J* 7.1 Hz, CH_3CH_2O), 4.09 (1 H, d, *J* 13.2 Hz, C*H*Ph), 4.43 (1 H, d, *J* 13.2 Hz, C*H*CN), 5.28 (1 H, s, C*H*Ph), 6.32br (1 H, s, NH), and 7.4 (10 H, m, Ph).

Preparation of Methyl 3-*Benzoyl*-1-*cyano*-4-*hydroxy*-2,4,6-*triphenylcyclohexanecarboxylate* (8).—This material was a side product of the condensation of methyl cyanoacetate with chalcone, which was performed for another study, m.p. 222—223° (lit.,[30] 226°), δ (5% $CDCl_3$) 2.21 (1 H, dd, *J* −14.5, *J* 3.3 Hz, H-5e), 2.99 (1 H, ddd, *J* −14.5, *J* 13, *J* 2.5 Hz, H-5a), 3.25 (3 H, s, CH_3O), 4.33 (1 H, m, H-6a), 4.35 (1 H, d, *J* 12 Hz, H-2a), 4.92 (1 H, d, *J* 12 Hz, H-3a), 5.31 (1 H, d, *J* 2.5 Hz, OH), and 7.0—7.7 (20 H, m, Ar).

Preparation of 4-*Cyano*-3,4,5-*triphenylheptanedioic Acid* (9).—This material was prepared by the method of Avery, m.p. 216—218° (lit.,[10] 218—219), δ (5% w/v C_5H_5N) 2.68 (2 H, dd, *J* −15.9, *J* 11.2 Hz, C*H*CO_2H), 3.31 (2 H, dd, *J* −15.9, *J* 2.7 Hz, C*H*CO_2H), and 4.00 (2 H, dd, *J* 11.3, *J* 2.7 Hz, C*H*Ph); the phenyl protons were obscured by solvent.

Preparation of 5-*Oxo*-2,3,5-*triphenylpentanenitriles* (10) *and* (11).—The compounds were made by the method of Avery and Jorgenson,[42,43] but separated by fractional crystallization by the triangle scheme using ether–light petroleum. The overall yield of the mixture of products was 22%, from which (10) (9%), m.p. 116—117° (lit.,[42] 118°), and (11) (5%), m.p. 107—108° (lit.,[32] 109°) were separated, plus other less pure fractions; δ (5% $CDCl_3$) for (10) 3.4—3.75 (2 H, m, CH_2), 3.84 (1 H, m, PhC*H*), 4.49 (1 H, d, C*H*CN), and 7.0—8.0 (15 H, m, Ph) [neither $Pr(dpm)_3$ nor $Eu(dpm)_3$ clarified the spectrum adequately]; δ ($CDCl_3$) for (11) 3.38 (1 H, dd, *J* −17.4, *J* 4.9 Hz, C*H*COPh), 3.71 (1 H, dd, *J* −17.4, *J* 8.8 Hz, C*H*COPh), 3.95 (1 H, m, C*H*Ph), 4.22 (1 H, d, *J* 6.0 Hz, C*H*CN), and 7—8 (15 H, m, Ph).

Preparation of 4-*Bromo*-5-*oxo*-2,3,5-*triphenylpentanenitriles* (12) *and* (13).—This compound was prepared by the method of Kohler and Allen:[35] (12) (14%), m.p. 168—170° (lit.,[33] 166°); (13) (6%), m.p. 129—130° (lit.,[33] 131°) (other less pure fractions were also obtained); δ (5% w/v $CDCl_3$) for (12) 3.84 (1 H, dd, *J* 11.4, *J* 4.2 Hz, CHPh), 5.06 (1 H, d, *J* 4.2 Hz, CHCN), 6.00 (1 H, d, *J* 11.4 Hz, CHBr), and 6.8—7.9 (15 H, m, Ph); δ (*ca.* 5% w/v $CDCl_3$) for (13) 4.08 (1 H, dd, *J* 4.8, *J* 10.6 Hz, CHPh), 4.48 (1 H, d, *J* 4.8 Hz, CHCN), 5.87 (1 H, d, *J* 10.6 Hz, CHBr), and 6.9—8.2 (15 H, m, Ph).

Preparation of 4,4-*Dicyano*-1,3-*diphenylbutan*-1-*one* (14).—The procedure of Kohler and Souther[43] was used to obtain the product, m.p. 124—125° (lit., 124—125°) in 85% yield, δ (2.5% $CDCl_3$) 3.66 (1 H, apparent d, CHCO), 3.68 (1 H, apparent d, CHCO), 3.93 (1 H, apparent dd, CHPh), 4.11 (1 H, d, *J* 5.0 Hz, CHCN), and 7.1—7.95 (10 H, m, Ph).

N.m.r. Spectra.—The n.m.r. spectra were run on a Varian XL-100 instrument (or in one case on a Varian A-60D instrument). The ^1H chemical shifts were determined from 500 Hz width traces using the LAOCON 3 program for spectrum simulation. The coupling constants were determined from 100 Hz traces. The program was adapted for a computer trace of the spectrum, and either the iteration mode was used, or a trial-and-error fit was attempted until the computer generated trace was superimposable on the original spectrum. For (1), (3), (5), and (11), the r.m.s. error using the iteration mode was 0.077, 0.102, 0.072, and 0.097 respectively. Certain spectra were not stimulated. In other cases, *e.g.* (15), (16), and part of the spectrum of (14), the spectra were first order due to large separations of the ^1H resonances. The 300 MHz spectrum of (10) was obtained from the Institute of Polymer Research, University of Akron.

The ^{13}C coupling constants were determined from 1 000 Hz spectral width determinations, using either a 2 s or more frequently a 4 s acquisition time. 5 000—10 000 Transients were collected. The spectra were simulated, but for these particular compounds, the deviation of the calculated coupling constants from the observed line separations was usually less than the error in data acquisition (either ±0.4 or 0.2 Hz). In most cases, as concentrated a solution as possible was used for the determinations (at least 0.3 g substrate per 3.0 ml solvent) and extreme filtering of the spectral acquisition was used in later runs. In our hands, the methoxycarbonyl groups in (1) and (2) gave unclear spectra difficult to interpret. The ketone carbonyl in (1) gave a triplet, which although clear, was not immediately assignable.

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