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STRUCTURES OF CYANOCYCLOPENTADIENES AND RELATED COMPOUNDS

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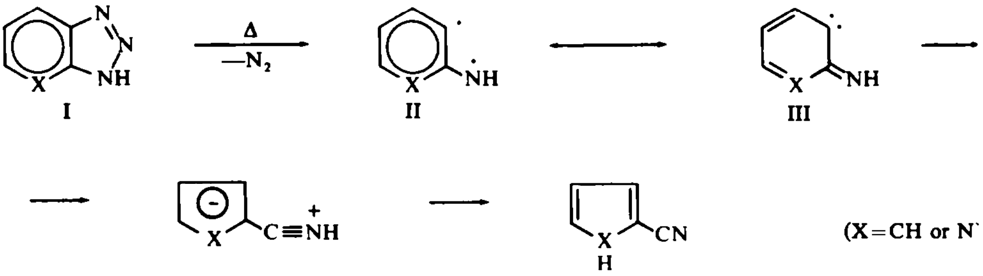
Abstract—Consideration of NMR spectral data, deuterium exchange experiments, and the mechanism of protonation of the anion lead to the conclusion that cyanocyclopentadiene exists mainly as the 1-cyano isomer. The structures of the methylcyanocyclopentadienes, the cyanoindenes and the cyanopyrroles are discussed in similar terms.

INTRODUCTION

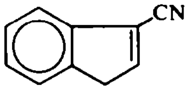
IN THE preceding paper[1] we described the ring contraction which occurs on pyrolysis of triazoloarenes (I) and proposed a mechanism involving rearrangement of the iminocarbenes (III), analogous to Wolff Rearrangement of the ketocarbenes.[2] Deduction of the mechanism depended upon correct structural assignments to the cyanocyclopentadienes (IV, X = CH) and cyanopyrroles (IV, X = N) encountered as end products. The coarse features of the rearrangement followed from three examples where the product was either known (V[3], VI[4]) or readily identifiable (VII), and was supported by the fact that triazolopyridines (I, X = N) apparently follow essentially the same mechanism.[1]



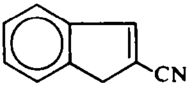
I II III IV

(X=CH or N)

V



VI



VII

Formation of cyanocyclopentadienes by azide pyrolysis[5,6] is complicated by group migration,[7] but they can be obtained pure by benzotriazole pyrolysis.[1] The structural assignments in these compounds are complicated by facile prototropic shifts, which occur more easily than in less acidic cyclopentadienes,[8,9] and by the ease with which

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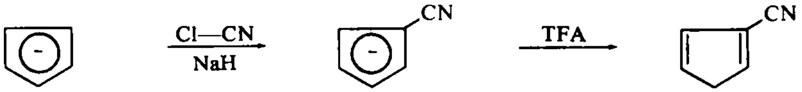
dimerization occurs. The compounds discussed in this paper were purified by GLC/low pressure distillation, and were stored under N_2 at liquid N_2 temperature, being raised to room temperature just prior to examination.

Cyanocyclopentadiene (IV, X = CH)

There is considerable chemical and spectroscopic evidence[9–12] to indicate that cyanocyclopentadienes bearing unsaturated substituents tend to exist mainly as the fully conjugated 1-derivatives, as would be expected from π-energy considerations. Peters[10] assigned the 1-cyano structure to IV (X=CH) on the basis of its UV spectrum. The results of Diels—Alder dimerization have in some cases been used to support the alternative 2-structures, but such methods are not a valid means of investigating tautomeric systems. For example, Mironov *et al.*[9] found that the rate of tautomerization in methyl- and deuterocyclopentadienes was faster than that of addition to a low activity dienophile (methylcyclopentadiene) but slower than that of addition to a high activity dienophile (maleic anhydride). Thus Peters[10] found that dimerization of cyanocyclopentadiene gave two dimers, as does also the product from benzotriazole pyrolysis.

Webster[3] prepared cyanocyclopentadiene by reaction of cyclopentadienide ion with cyanogen chloride, followed by protonation. A study of protonation of cyanocyclopentadienide in TFA was stated to give the 2-cyano isomer, the unexpected site of protonation being tentatively ascribed to kinetic control. The NMR spectrum of the product was stated to agree best with a calculated spectrum of 2-cyanocyclopentadiene. While the structure of cyanocyclopentadiene itself was of no mechanistic significance to us, the correct assignment of chemical shifts in this compound was of critical importance, forming the basis of structural assignments in substituted derivatives. The identity of our material with that of Webster was readily established from spectroscopic data.[1] The NMR spectrum in TFA was as described,[3] although the splittings were slightly more complex. The UV spectrum was also the same, although the extinction coefficient was higher* than reported by either Peters[10] or Webster,[3] and the UV spectrum in alkali agreed with that reported[3] for the potassium salt. As a final check, our material was recovered from the sodium salt with TFA at −50 to 0°, and the IR and UV spectra were shown to be the same as the starting material.



The 100 Mhz NMR spectrum of cyanocyclopentadiene is shown in Fig 1, the protons and their signals being designated A,B,C and X_2 in order of increasing field. The position of X_2 leaves no doubt as to its identity with the CH_2-signal.

Peak A is a quintet (coupling with B,C and X_2), reduced to a triplet by irradiation of X_2 (two weaker lines, probably due to another tautomer, remain at 1 hz lower field). Irradiation of B/C similarly reduces it to a triplet, but accurate measurement is impaired by proximity of the signals. $J_{AC} = J_{AB} = J_{AX} = 1{\cdot}5$ hz.

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* Our results were for freshly distilled samples, forming fine colourless needles m.p. −45 to −42°. The extinction coefficient[1] falls with time, due to dimerization, and our own results may also be low on this account.

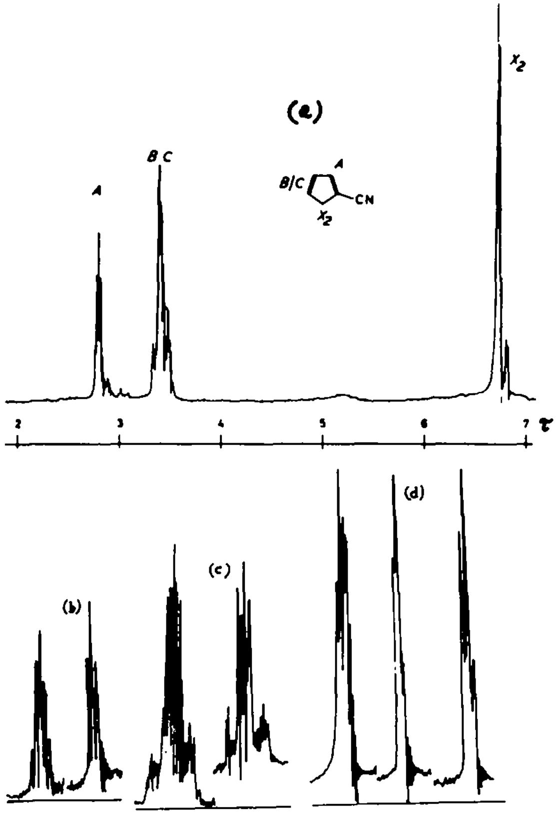
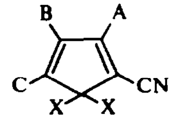


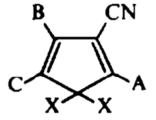
FIGURE 1. (a) 100 MHz SPECTRUM OF CYANOCYCLOPENTADIENE
(b) H_A - 250 Hz SWEEP WIDTH, NORMAL AND X_2-IRRADIATED
(c) H_{BC}- 250 Hz SWEEP WIDTH, NORMAL AND X_2- IRRADIATED
(d) X_2 - 250 Hz SWEEP WIDTH, NORMAL, H_A- AND H_{BC}- IRRADIATED

Peak X_2 is an unsymmetrical quintet, collapsing to an unsymmetrical triplet on irradiation of A ($J_{XB} = J_{XC} = 1$ hz). Irradiation of B/C collapses X_2 to a doublet ($J_{AX} = 1 \cdot 5$ hz. Again, a second doublet remains at about 20% the intensity of X_2, indicating a second tautomer).

Peak B/C should consist of two doublets if they are due to H_3 and H_4, and this is the pattern observed in TFA solution, where each doublet (with fine splitting) integrates at one proton ($J_{BC} \sim 6$ hz). In carbon tetrachloride the chemical shifts are so close that the pattern becomes unintelligible; on irradiation of X_2, however, the system reduces to two sets of doublets ($J_{BC} = 5 \cdot 7$ hz).

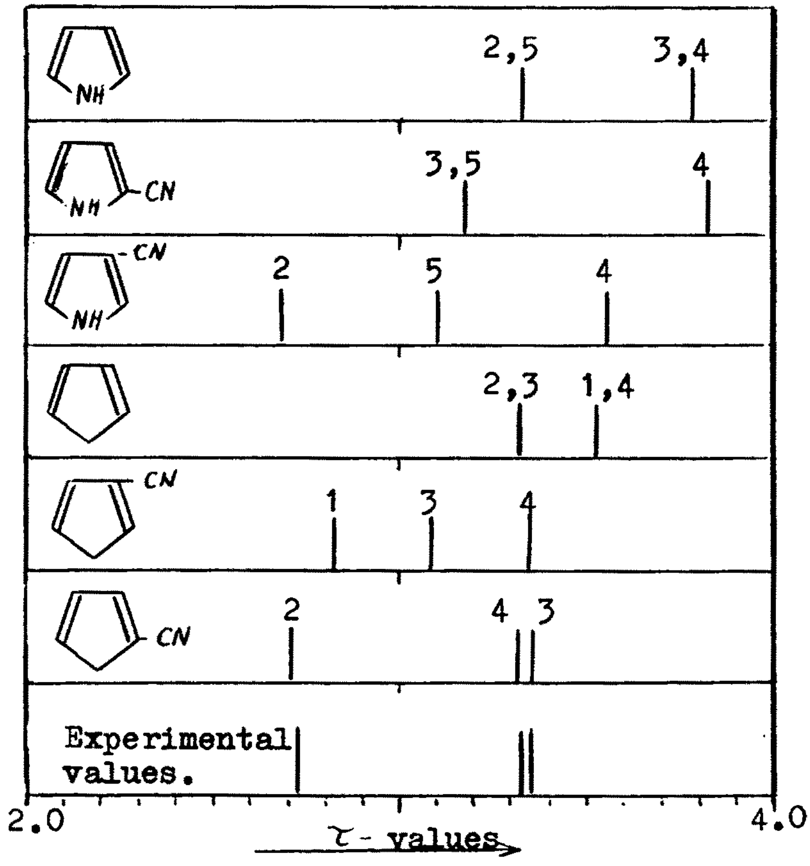


VIII



IX

These results are interpretable in terms of either structure VIII or IX, although the chemical shifts tend to favour VIII. In IX, H_A and H_B are both under the influence of the cyano group, and it is difficult to envisage either of them coinciding with H_C in chemical shift, i.e. we would expect *two* low-field protons or three separated peaks. The argument is better illustrated in Fig 2, where the spectra of VIII and IX are simulated by applying to cyclopentadiene the chemical shift increments observed on substituting CN-groups into pyrrole.[13] The prediction for VIII is in surprisingly good agreement with the experimental figures. On the other hand, the predictions for IX bear little relation to the spectrum in Fig 1, and constitutes further evidence for rejecting this structure.



* Essentially the same conclusions may be reached by carrying out the same comparison for the cyanofurans and cyanothiophenes (cf. ref. 24).

FIG. 2 Chemical Shifts for Cyanopyrroles and Estimated * Shifts for Cyanocyclopentadienes.

Diamagnetic anisotropy corrections for CN *in* VIII *and* IX. The Δ τ values observed on substitution of CN in cyclopentadiene consist of the electronegativity contribution and the anisotropy effect of CN. The latter were calculated by the method of Reddy and Goldstein[14] for VIII, and are listed in Table 1. It will be seen that the shielding of a proton α- to CN is ~ + 0·2 ppm, and ~ + 0·1 ppm for β- or γ-protons. The shielding of H_5 in VIII is + 0·23 ppm,* while the effect on Me groups is small enough to be neglected. The

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* This is much the same as for H_2, i.e. H_5 can effectively be regarded as an α-proton in VIII. Since the anisotropy effects depend only on geometry, this permits the application of Table 1 to IX (with appropriate renumbering). Thus H_5 in IX is treated as a β-proton, with $\Delta\delta = 0{\cdot}1$ p.p.m.

calculations for VIII constitute a logical set, with the effect on H_2 and H_4 (conjugated with CN) substantial, and relatively small on H_3. In the case of IX, the calculated effect on H_3 seems disproportionately small compared to that on the more distant H_5, and it is not reasonable that it should be less than on the more distant (and similarly unconjugated)H_4. In summary, structure VIII again appears a better interpretation of the experimental results than structure IX.

TABLE 1. DIAGMAGNETIC ANISTROPY CORRECTIONS IN CYANOCYCLOPENTADIENE VIII

			$-\Delta\omega^{d}$(hz)		$-\Delta\delta$
Group	$\alpha^{\circ b}$	R(A°)[c]	100 Mhz	60 Mhz	(ppm) ± 0·05
H_2	41·056	3·218	19·358	11·606	0·194
H_2	15·177	5·221	11·524	6·909	0·115
H_4	13·210	5·336	11·089	6·649	0·111
H_5	36·152	3·379	22·646	13·578	0·226
2-CH_3	53·343	3·606	1·349	0·809	0·01
3-CH_3	18·339	5·987	7·253	4·349	0·07
4-CH_3	15·687	6·119	7·104	4·254	0·07
5-CH_3	46·159	3·771	7·487	4·489	0·07

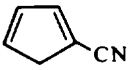
[a] microwave[15] and crystallographic[16] data averaged to give a symmetrical ring. Other data used: C—H, 1·08 A°; C—H, 1·09 A°; C—CH_3, 1·543 A°; C—CN, 1·426 A°; C≡N, 1·164 A°; $C_5C_1(CN) = (NC)C_1C_2 = 125{\cdot}35°$; $\widehat{C_1C_2H_2} = \widehat{H_2C_2C_3} = 125{\cdot}3°$; $\widehat{H_5C_5H'_5} = 116{\cdot}2°$. Methyl protons were regarded as time-averaged at 1·906 A° from the ring carbon atom.

[b] angle between C≡N bond axis and the line joining H to midpoint of C≡N.

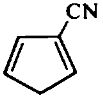
[c] distance between H and the midpoint of C≡N.

[d] $\Delta\omega = \Delta\chi(3\cos^2\alpha - 1)/3R^3$, $\Delta\chi = -16{\cdot}5$ cm³/mole.

Subtraction of the measured chemical shifts (corrected for anisotropy contributions) from those for cyclopentadiene give the electronegativity contributions below.



VIII



IX

Protonation of cyanocyclopentadienenide ion. In order to test Webster's[3] hypothesis that protonation of cyanocyclopentadiene might be kinetically controlled, we repeated the protonation experiments at low temperature, using deuterosulphuric acid. The nitrile was rapidly isolated at 0°, and the 100 Mhz NMR spectrum was measured in carbon tetrachloride. Three bands were observed as before, but the integration ratio A : B/C : X_2 was 0·82 : 2·04 : 1·14 instead of the expected 1 : 2 : 1 (which should result regardless of whether X or XI is formed). It was evident that D-shifts had occurred at some stage. The possibilities of D- and H-shifts in X and XI are set out in Chart 1. If we assume that the NMR spectra of VIII and IX are such that a mixture might escape detection, the apparent changes in the A : B/C : X_2 ratio can be calculated. If X were formed initially, the ratio would subsequently tend towards 1·0 : 1·5 : 1·5, which is in the wrong direction. Alternatively, initial formation of XI, followed by tautomeric shift, would move the ratio

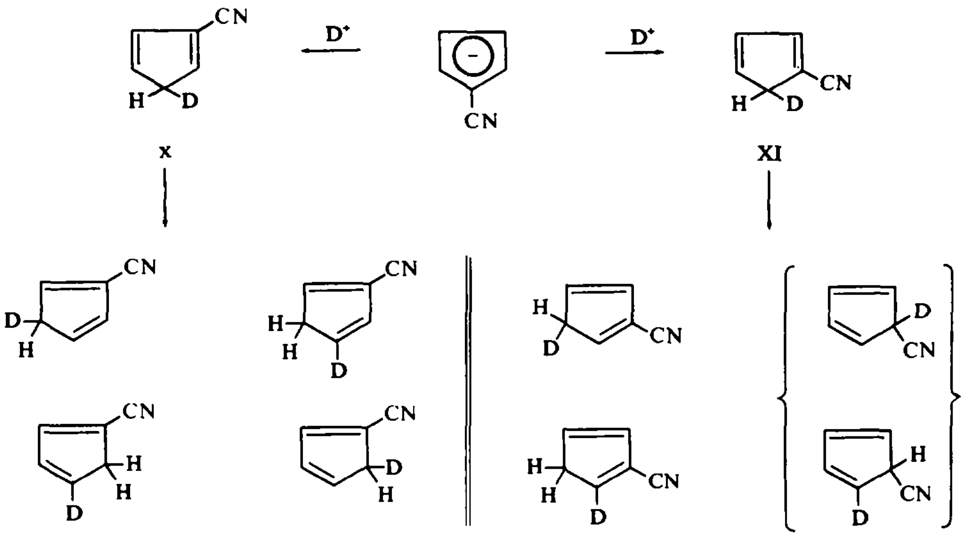
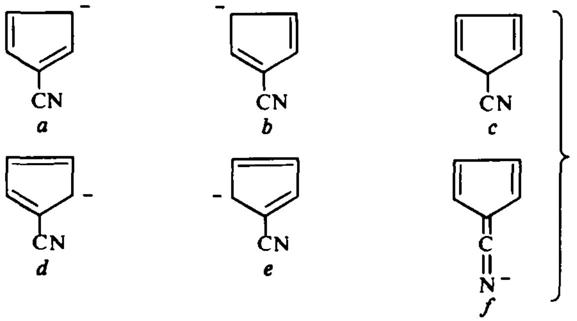
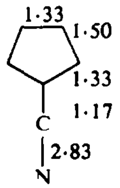


CHART I

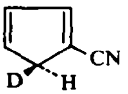
towards 0·67 : 2·0 : 1·33, which is in the direction observed. Since the D/H-scrambling was incomplete, and the ratio did not change over twelve hours at 20–34°, it follows that the shifts occurred during the quenching of the anion in deuterosulphuric.

The initial site of deuteron capture by the anion may be deduced by application of the principle of least motion.[17] The cyanocyclopentadienide ion XII has six contributing structures (*a*–*f*) and the bond orders may be approximated by the method of Pauling,[18]



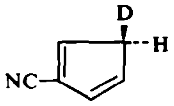


XII



Σ(bond order)^2 = 1·56

XIII

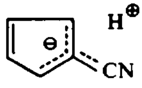


1·22 ·

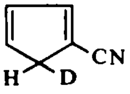
XIV

0·89

XV



XVII

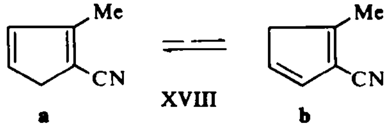


XVI

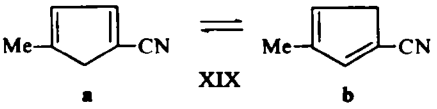
assigning equal weight* to a–f. The sum of the squares of the bond order changes leading to XII, XIV and XV can now be approximated as 1·56, 1·22 and 0·89 respectively. Thus the preferred site of protonation should be at the CN-bearing carbon, as would be deduced from the Hughes–Ingold rule[19] (XV being the strongest acid and least stable tautomer). A subsequent D-shift in XV would lead to 1-cyanocyclopentadiene-5-d_1 (XVI). Although this is a symmetry allowed 1,5-shift, we would not consider this a necessary condition in XV, particularly under the conditions of the experiment. The cyanocyclopentadienes are relatively strong acids, and can be estimated[3] to have a p*Ka* ~1 in aqueous solution—it is probable that a considerable degree of ionic character enters into the migration process. The migrating proton (deuteron) should remain in the vicinity of the electron-rich C–CN centre (XVII), i.e. more direct exchange between X_2 and A protons would be favoured over X_2/BC exchange, as in the concerted 1,5-shifts.

From both the experimental and theoretical points of view it seems that the product isolated from benzotriazole pyrolysis can be assigned the structure 1-cyanocyclopentadiene VIII, and that this is the thermodynamically stable isomer. We have indicated that another tautomer is present to some extent, and this must be 2-cyanocyclopentadiene IX. The presence of a small shoulder on the high frequency side of the methylene peak, ascribed by Webster[3] to the other isomer, is due to dimer formation, and increases with time (up to 50% dimerization in CCl_4 over 12 hr).

Methylcyanocyclopentadienes. If we assume that the conclusions reached above are correct, then the structures assigned to the methylcyanocyclopentadienes are self-evident. The NMR spectra are shown in Fig 3. The two isomers XVIII and XIX elute close together on GLC, and both give broad, tailing peaks due to dimerization and dedimerization in the column and in the injection port. Thus each spectrum shows traces of the other isomer, which can only be eliminated by repeated GLC. It can be seen from Fig 3 that a Me group to some extent counterbalances the effect of CN, but the spectrum of XVIII shows two low field protons at very similar chemical shifts, which is not consistent with the tautomer (b). Apparently the 1-cyano isomer is almost exclusively present. The Me signal is primarily a triplet (J = 2 hz), due either to coupling with H_3 and H_4 (*cf* methylthiophenes[20]) or to homoallyic coupling with CH_2, as was found[21] in 1,2,3-trimethylcyclopentadiene (J = 1·8 hz). The complexity of the CH_2 signal suggests that it is coupled to H_3, H_4 and Me_3. In the spectrum of XIX, signals can be seen for both tautomers *a* and *b*. Both Me signals are doublets (with fine structure) due to allyic coupling (J = 1·5 hz), the major signal being assigned to the hyperconjugated XIX a.



XVIII



XIX

2-, 3-, 4(7)- *and* 5(6-) *Cyanoindenes.* Structural assignment in this group of compounds was partly simplified by the availability of authentic 3-cyanoindene[4] and by the characteristic differences in D/H exchange between the cyanocyclopentadienes XX–

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* If the forms *d,e,f* are assigned twice the weight of *a,b,c* due to having the CN conjugated with the dienoid system (*d,e*) or the charge on the most electronegative atom (*f*), XV still emerges with the lowest Σ value.

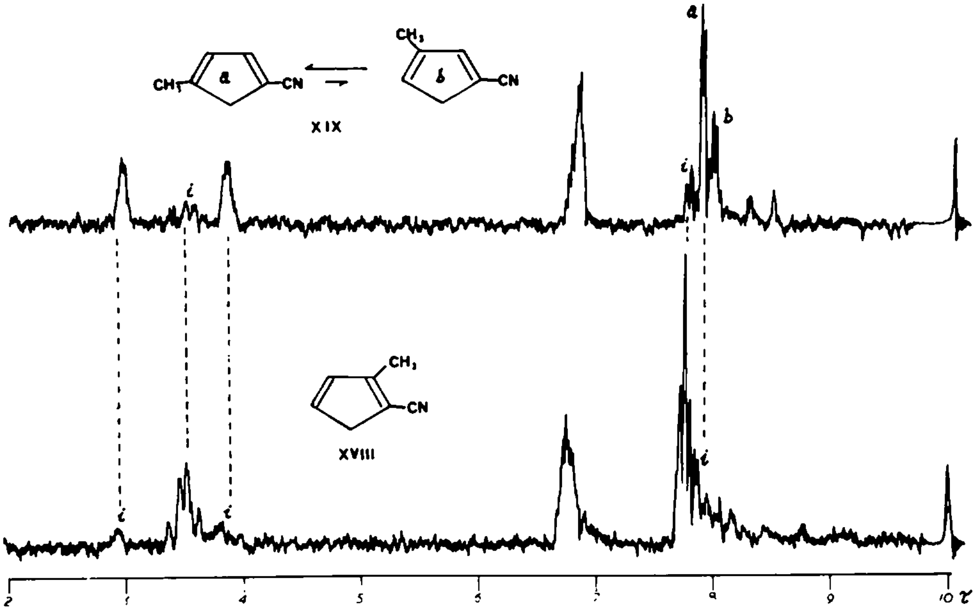
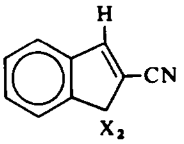
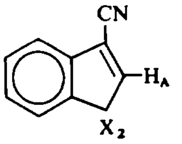


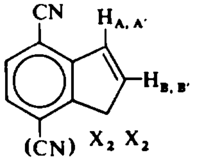
FIG. 3 100 MHz NMR Spectra of the Methylcyanocyclopentadienes. ("i" represents signals due to the other isomer in each trace).



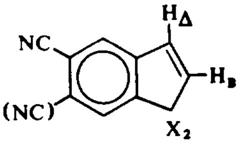
XX



XXI



XXII



XXIII

XXI and the benzonitriles XXII–XXIII. The first pair rapidly incorporated D in the inlet system of the MS10C2, and exchanged 3H with Et_3N/D_2O, whereas the second pair did not exchange in the inlet system, and incorporated up to 4D with Et_3N/D_2O, thus indicating an unsubstituted 5-membered ring.

Fig 4

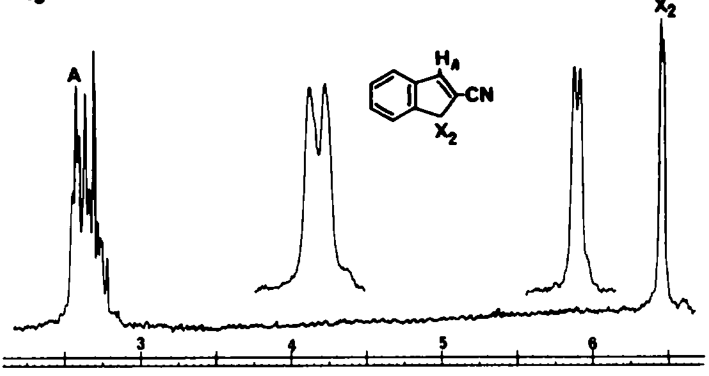


FIG. 4 100 MHz Spectrum of 2-Cyanoidene. The X_2-signal is also shown at 500 and 250 Hz sweep width.

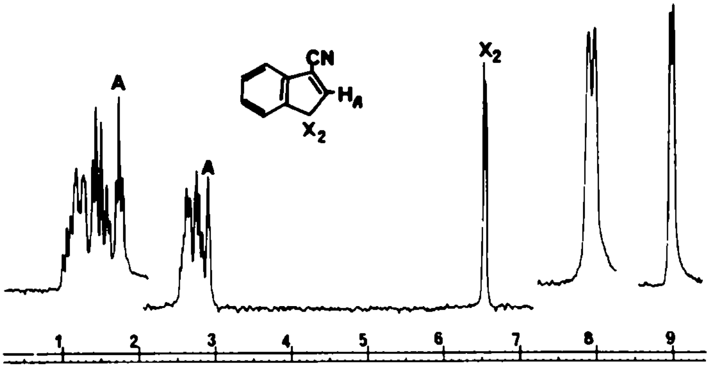
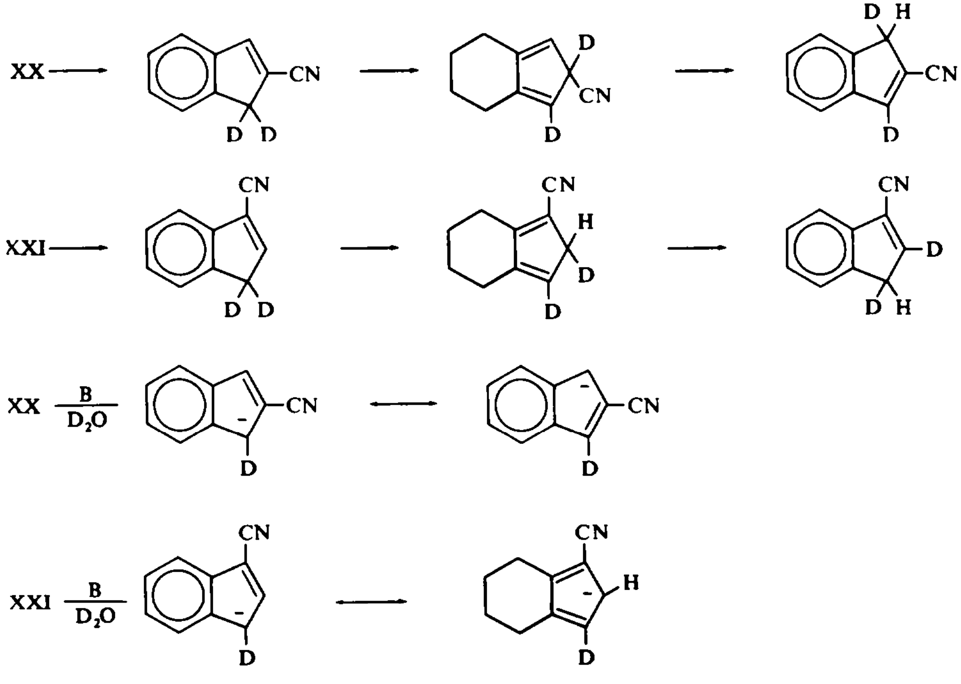


FIG. 5 100 MHz NMR Spectrum of 3-Cyanoindene. The X_2-signal is also shown at 500 and250 Hz sweep width.

The 100 Mhz NMR spectra of XX and XXI are shown in Figs 4 and 5 respectively. The 2-cyanoindene (XX) H_A is identified as the triplet at τ 2·57 by irradiation of X_2, which collapses it to a singlet; the X_2 doublet is similarly reduced to a singlet by irradiation at τ 2·57 ($J_{AX}=2$ hz). In 3-cyanoindene(XXI) H_A is seen as a triplet at τ 2·91, and double irradiation again confirms $J_{AX}=2$ hz. It is known that the coupling constants between the two vinylic protons and the methylene group in indene are equal and of opposite sign.[22] The rates of D/H exchange in XX and XXI were also diagnostic. In the MS10C2 inlet system XX exchanged 2H rapidly, but the third only slowly, whereas XXI rapidly exchanged 3H. The proposed mechanisms for the incorporation are shown in Chart 1. In 2-cyanoidene (XX) the third D can only be incorporated after a series of 1·5-shifts passing through an unconjugated 2-cyanoisoindene, whereas in XXI



the conjugation with the CN group is retained in the 3-cyanoisoindene. The reverse situation attains in base-catalysed exchange, where XX incorporates 3D faster than XXI. In the repective anions it can be seen that XXI must react in an isoindenoid form to effect full exchange, whereas XX retains the stable benzenoid structure throughout.

4(7)-Cyanoidene XXII and 5(6)-cyanoidene XXIII forms two tautomeric pairs, each eluting as one peak on GLC. Both had ν_{CN} 2231 cm^{-1} (XXI: $\nu_{CN} = 2231$ cm^{-1}. The fully conjugated XX showed $\nu_{CN} = 2215$ cm^{-1}) had UV spectra very similar to that of indene itself, and had mass spectra identical with those of XX and XXI. The distinction between them was based on the 100 Mhz NMR spectra shown in Figs 6 and 7–the 4-/7-pair XXII showed greater chemical shift differences for the two tautomers than the 5-/6-pair XXIII. The protons of 7-cyanoinene are labelled A,B,X_2 and those of 4-cyanoindene are labelled A′, B′, X'_2. No distinction is possible for 5- and 6-cyanoindene. In the spectrum of XXII, X_2 can be seen at 250 hz sweep width to consist of a triplet at slightly lower field than X'_2 due to the *o*-CN group, whereas X'_2 is seen as a triplet of doublets due to coupling with H_7.[23] The complex bands at τ 2·9–3·6 are assigned to A′B′ and AB. In Fig 6(c) the lines 1–4 constitute a pair of doublets (H_A, H_B), each peak being split into a triplet by coupling with X_2. Lines 1′-4′ constitute the same system for 4-cyanoindene. Irradiation of X_2 reduced lines 1-4 to the expected pair of doublets, while irradiation of X'_2 reduced lines 1′-4′ similarly, but each line remained finely split, again due to coupling with H_7. With this interpretation the chemical shifts and coupling constants in Fig 6 can be assigned as follows:

7-Cyanoindene: H_A 3·16, H_B 3·38, X_2 6·48 • $J_{AB} = 5{\cdot}5$ hz, $J_{AX} = J_{BX} = 2{\cdot}0$ hz.

4-Cyanoindene: $H_{A'}$ 2·97, $H_{B'}$ 3·28, $X_{2'}$ 6·58 • $J_{A'B'} = 5{\cdot}5$ hz, $J_{AX} = J_{B'X'} = 2{\cdot}0$ hz, $J_{A'H7} = J_{X\ H7} = 1$ hz.

The spectrum of 5(6)-cyanoindene (Fig 7) shows the X_2-signals at almost the same chemical shift; at a sweep width of 100 hz they are recognizable as two triplets. The vinylic proton pattern has not been elucidated, but deuteration with alkaline D_2O resulted in (mainly) a trideuterated species which gave the spectrum in Fig 7(b). The two near-singlets at τ3·36 and 3·44 are presumed to be H_B protons.

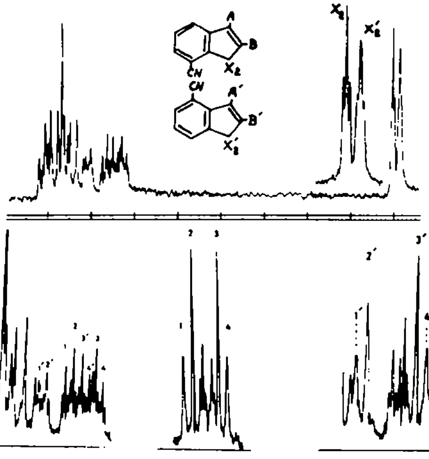


FIG. 6 100 MHz NMR Spectrum of 4(7)-Cyanoindene at 500 Hz sweep width. The region 2.4-3.5 is shown at 250 Hz sweep width, with the successive effects of irradiation at 6.48 (X_2) and 6.58 (X'_2).

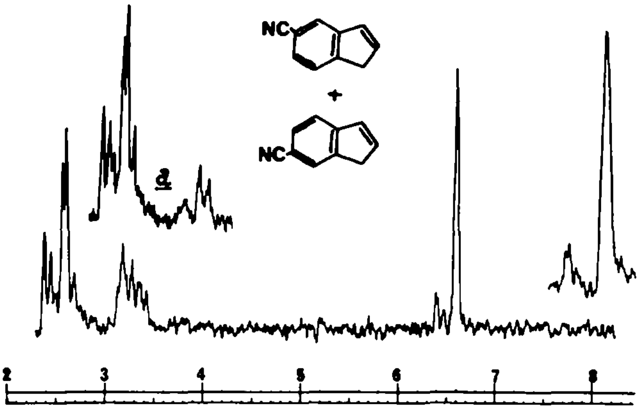


FIG. 7 100 MHz NMR Spectrum of 5(6)-Cyanoindene (X_2 also at 500 Hz sweep width) (a) Effect of irradiation of X_2 at 6.60.

EXPERIMENTAL

Protonation of cyanocyclopentadiene. To a mixture of sodium hydride (0·48 g, 0·02 mole) in anhyd ether (10 ml) maintained under N_2 at −80°, was added cycanocyclopentadiene (freshly distilled, 1·82 g, 0·02 mole) in anhyd ether (10 ml). Dry THF (5 ml) was added and the mixture stirred at room temp for 1 hr, when H_2 evolution had ceased. The soln was cooled to −50°, acidified with TFA (1·7 ml in 10 ml ether), and extracted with water at 0°. The ether phase was washed twice with water at 0°, dried over $MgSO_4$ and evaporated at −10 to 0°. The IR and UV spectra of the product were identical with those of the starting material.

1-*Cyanocyclopentadiene*-5-d$_1$ (X). The Na salt was prepared as described above from 1·75 g cyanocyclopentadiene, and the THF/ether soln was treated with 2M D_2SO_4 in D_2O (99·9%, 10 ml). The organic layer was evaporated below 0° *in vacuo.*, the residue extracted with dry ether and dried over $MgSO_4$ at −10°. Removal of the ether at 0°, and high vacuum distillation of the product (50° bath) gave X, which was degassed and dissolved in CCl_4 for NMR and IR spectroscopy. IR (CCl_4): 3080 m, 2980 m, 2940 m, 2900 m, 2215 vs, 1620–1600, 1498 s (shoulders at 1485 and 1510), 1370 s, 1360 s, 1350 m, 1230 s, 1165 s, 1155 s, 1080 m, 1020 s, 1005 m, 990 m, 900 s, 840 s, 670 s cm^{-1}.

Base-catalysed D- *exchange in cyanoindenes.*

(1) The inlet system of the MS10C2 mass spectrometer was saturated with D_2O overnight, and D-incorporation was followed by scanning the molecular ion repeatedly. 2-Cyanoindene rapidly showed an M+2 peak, but the M+3 peak appeared only slowly. 3-cyanoindene under the same conditions rapidly showed M+3, while 4(7)- and 5(6)-cyanoindenes, like indene itself, did not show any mass increase in several hours at 150°.

(2) An ethereal soln of 2- and 3-cyanoindenes was shaken with Et_3N/D_2O for 18 hr at room temp, the products separated by GLC on a D_2O-treated column (Carbowax 20M) and examined by mass spectrometry. The isolated 2-cyanoindene showed complete incorporation of 3D, whereas that in 3-cyanoindene was incomplete.

(3) 4(7)-Cyanoindene and 5(6)-cyanoindene, treated as in (2) above, yielded mixtures of deuterated species containing up to 4D. The main species (80%) contained 3D.

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