Spin Delocalization in 7-Norbornenyl-Type Radicals. 2.[1] The Effect of 7-Substitution on Stereochemistry

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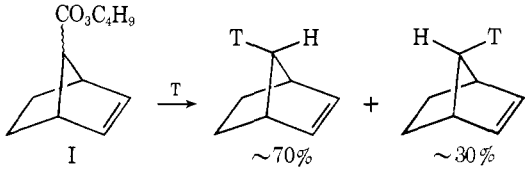
Abstract: Contact shifts have been studied for a series of 7-azabenzonorbornenes and norbornadienes and compared with those of model compounds of known structure. It has been concluded that for the secondary amines the N–H bond lies anti to the benzene ring while methyl substitution at nitrogen causes an inversion of the conformational populations. In view of these changes upon minor substitution it is advised that caution should be exercised in interpreting results for similar systems in terms of substantial bishomoconjugative stabilization. From an examination of the contact shifts for the vinylic protons it is suggested that some bishomoconjugative delocalization may occur but that the accompanying stabilization is minimal.

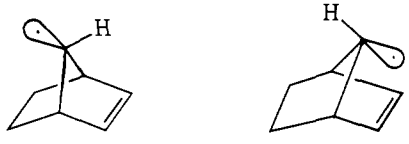
There has been considerable recent interest in the structure of the 7-norbornenyl radical and related species with particular reference to the orientation of the nonbonding orbital.[1,2] This subject is pertinent to the importance of bishomoconjugation and its influence on the stereoselectivity, etc., in the reactions of these species.

In a thorough study of the behavior of the 7-norbornenyl radical, Kochi, Bakuzis, and Krusic[2h] found that the photolysis of either *syn*- or *anti-tert*-butylperoxy 7-norbornenecarboxylate, I, under a variety of conditions yielded products in which



I ~70% ~30%

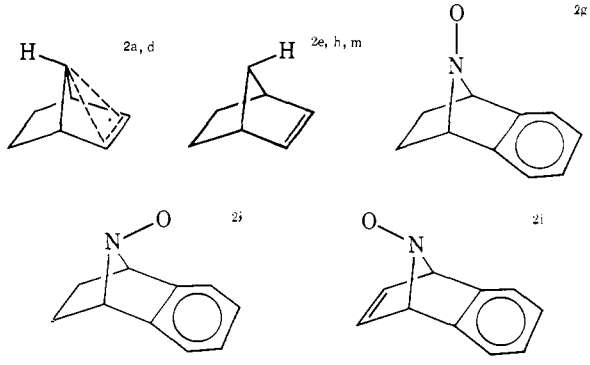
the radical was trapped predominantly from the anti side. This preferred attack anti to the double bond might be interpreted either in terms of the conformation II with subsequent reaction occurring at the front lobe of the nonbonding orbital or as a protection of the syn side by some form of interaction with the double bond III reminiscent of that observed in the corresponding cation.[3]

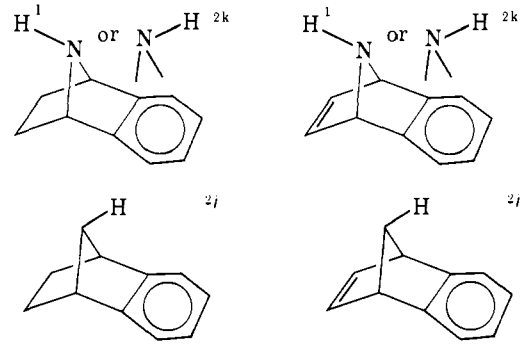


II III

A critical study of the ESR spectrum of the radical involved led the authors to conclude however that the larger lobe of the nonbonding orbital was disposed away from π cloud, a conclusion in keeping with earlier MINDO-1 calculations.[2m]

In related systems differing interpretations have been made and the following preferred conformations have been proposed by various authors:





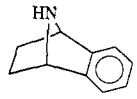
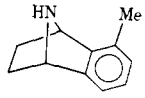
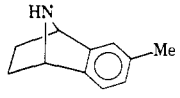
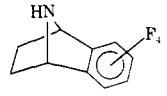
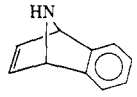
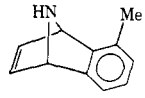
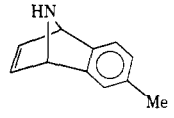
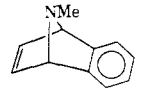
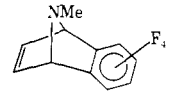
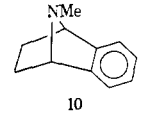
These assignments were based primarily on ESR data, sometimes with reference to INDO spin density calculations,[4] but this method is not without its difficulties. First, whereas the calculations give both the sign and magnitude of the spin densities, ESR yields only the magnitude and thus only half the information provided by the calculations can be utilized in the comparison with experiment. On occasion this difficulty can be circumvented by, for example, variable temperature ESR studies[2h] or by the appropriate CIDNP experiments.[5]

Second, the INDO method, by virtue of its approximate nature, does not always provide an unequivocal solution to the problem. Thus, in one instance,[2i] the stereochemical assignment had to be based upon a comparison of the experimental hfsc's of 0.82, 1.67, and 0.82 G with the two alternative sets of values, 0.2, 2.0, and 0.4 G or 0.2, 0.7, and 0.4 G, a difficult choice, particularly in view of the fact that one of these numbers falls in that region of conformational hyperspace in which agreement between INDO spin densities[6] and both experiment[7] and more refined calculations[8] is known to be poor.[7]

Frequently, the availability of the experimental sign of the spin density will greatly facilitate not only the stereochemical assignments but also provide useful information as to possible modes of spin delocalization. We have therefore used the NMR contact shifts induced in amines by nickel bisacetylacetonate[9] to study the 7-norbornenyl system. This method which introduces unpaired electron spin into the nitrogen nonbonding orbital leads to spin densities closely parallel to those in the corresponding hydrocarbon radicals[10] but has the advantage over ESR of directly yielding the signs as well as the relative magnitudes of the spin densities. It is shown here that this information is practically indispensable to structure determinations of this kind and that it also provides a useful insight into the mechanisms by which spin might be delocalized to the double bond.

Table I shows the contact shifts[11] obtained for a series of 7-azabenzonorbornenes and -norbornadienes.[12] Since the contact shift of a given nucleus is directly proportional to the spin density at that nucleus, the signed numbers may be re-

Table I. Contact Shifts[a] for 7-Azabenzonorbornenes

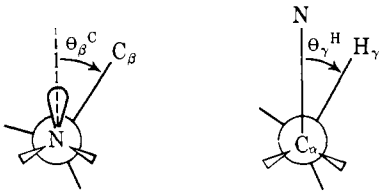
Structure	Reference shift	β protons bridgehead	γ protons		
			Vinylic	Exo	Endo
 1	−94[b]	+13.4 ± 4.6[c]		−2.8 ± 0.8	+9.5 ± 1.7
 2		+13.4[b]		−3.75 ± 0.38	+12.6 ± 1.8
 3		+13.4[b]		−5.33 ± 1.4	+8.49 ± 1.9
 4		+13.4[b]		−6.27 ± 1.3	+8.8 ± 0.9
 5	−94	+10.5 ± 2.5	+12.2 ± 2.7		
 6	−94	+14.7 ± 3.6	+8.7 ± 2.0		
 7	−94	+31.3 ± 3.5	+16.9 ± 1.9		
 8[d]	+50	+9.5 ± 0.8	−21.3 ± 1.0		
 9	+50	+15.0 ± 5.5	−20.0 ± 11.5		
 10	+50	+7.2 ± 0.4		−11.7 ± 0.8	−11.1 ± 1.4

[a] The shifts are obtained as the slopes of the lines for plots of chemical shift vs. [Ni]/[amine] for at least six different nickel concentrations. [b] Reference shift values were assigned in the following manner: All NCH_3 protons were assigned the value +50 and all NH protons −94, since it has been found $\Delta_{NCH_3}/\Delta_{NH} = 0.53 \pm 0.16$;[23] where neither NH nor NCH_3 proton shifts could be measured, primarily due to excessive line broadening of the former, this difficulty was circumvented by assigning the bridgehead protons the same value as for 7-azabenzorbornene itself. Since only the relative shifts are significant, these assignments are made solely for the readers' convenience. [c] Uncertainties quoted are standard deviations obtained in a linear least-squares regression analysis. [d] At 35 °C only one absorption (δ 2.11) was evident for the *N*-methyl protons. Morishima[2k] reports two peaks (δ 2.36, 2.60) at 24 °C although the assignment of these two peaks is not clear. The spectrum (Figure 4) and $Eu(fod)_3$ data (Table IV) show the dominant isomer to have the methyl group anti to the benzene ring. By contrast ^{13}C and $Eu(fod)_3$ discussions conclude it to be predominantly syn; Table I, 94% syn; and the equilibrium, 80% syn.

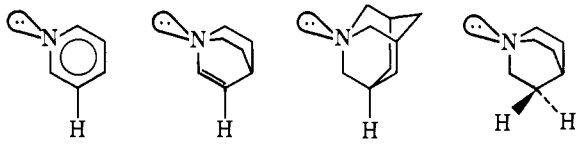
garded as relative spin densities at the various protons. From an examination of the relative shifts for the γ protons (exo, endo, and vinylic) it is clear that the compounds fall into two distinct categories: those having *one* large *positive* shift (endo or vinylic hydrogen) and those having *only* large negative shifts. It is also apparent that the only structural feature common to all members of one group is the N-methyl, a feature totally absent from the other group. Based upon arguments presented earlier[1] we propose that in these 7-unsubstituted amines the hydrogen is disposed anti to the benzene ring and in the 7-methylamines the CH_3 is syn.[13]

This assignment gains overwhelming support from a comparison of these shifts with those obtained for model compounds and from our knowledge of spin delocalization mechanisms. It is useful to discuss the exo and endo hydrogens and the syn and anti disposition of the lone pair in terms of the two

dihedral angles defined in the following Newman projections:[15]

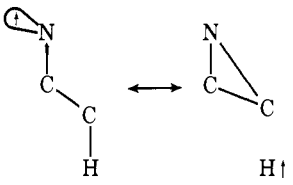


such that the four N-C-C-H orientations can be described by (θ_β^C, θ_γ^H): syn-endo, (60°, 150°); syn-exo, (60°, 270°); anti-exo, (180°, 90°); and anti-endo, (180°, 150°). For the anti-endo protons we have several models:



+31[7] (180°, 180°) | +32[7] (180°, 180°) | +25[7] (180°, 180°) | +3.2[7] (180°, 120°)

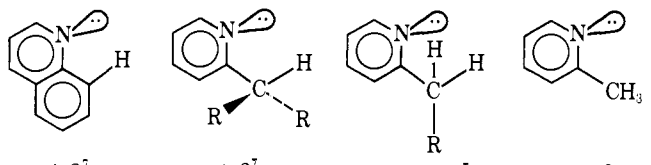
The large positive spin densities associated with the (180°, 180°) geometry arise from homohyperconjugation, IV,[7,17]



IV

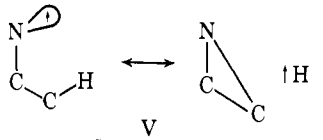
and are very sensitive to changes in θ_γ^H, falling off approximately as $\cos^6 \theta^H$.[6,7] Consequently a value of +10 to +12 is exactly as would be expected for (180°, 150°).

For the syn-exo proton (60°, 270°) it is somewhat more difficult to find suitable models but



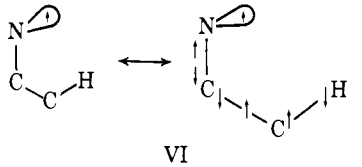
+8[7] (0°, 0°) | +3[7] (0°, ≃0°) | −5 to −10[7] (0°, ≃60°) | −11.4[7] (0°, FR)

are helpful. Two mechanisms appear to contribute to the shifts in this region: (a) a hyperconjugative interaction V,



V

in the region (0°, 0°),[7,20] accounting for the positive values, which falls off rapidly with θ_γ^H (and θ_β^C) and (b) spin polarization VI,



VI

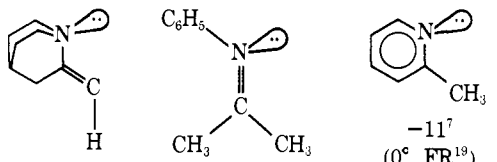
which makes the major (negative) contribution outside this region.[6,7,17] For (60°, 270°) a value of ca. −10 would be expected; the observed value is −12.

The syn-endo proton (60°, 150°) is in a region of negative spin densities relatively insensitive to conformational change[6,7] consistent with the dominance of spin polarization. As models,

Table II. Dihedral Angles θ_β^H and Nonplanarity at Nitrogen as Determined for the 7-Azabenzonorbornenes

Compd	θ_β^H, deg	θ_N,[a] deg
1	+69 ± 7[b]	+43 ± 13
5	+71 ± 4	+39 ± 8
6	+67 ± 5	+46 ± 10
7	+58 ± 6	+61 ± 12
8	−72 ± 1	−37 ± 2
9	−67 ± 5	−46 ± 10
10	−74 ± 1	−34 ± 2

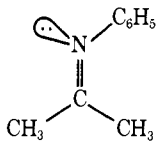
[a] θ_N is the angle between the C_1–N–C_4 plane and the nitrogen-substituent bond. [b] A positive sign indicates that the lone pair is directed toward the benzene ring. The quoted uncertainties derive directly from the uncertainties in the relative shifts of the bridgehead and reference protons.



−9[7] (0°, 180°) | −13[16] (0°, FR) | −11[7] (0°, FR[19])

accord with the observed value of −11.

And finally the anti-exo protons (180°, 90°) are in a region where spin polarization again dominates.[6,7] Although insufficient models are available,

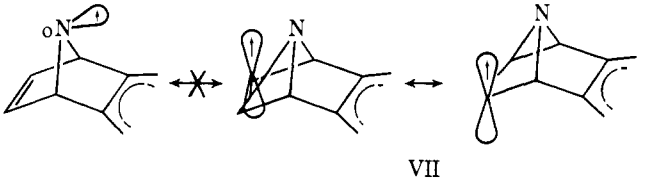


−12.5[15] (180°, FR[18])

indicates that the assigned values of −3 to −6 are quite appropriate. Alternative stereochemical assignments would be totally indefensible.[21] Furthermore, reference to Table I illustrates most forcefully that any attempt to assign stereochemistry in these systems without recourse to the experimental *signs* of the spin densities would have been a most difficult task.

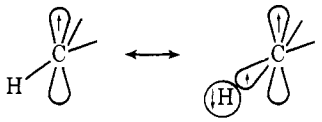
Having used the γ-hydrogen shifts to establish gross invertomer populations[13] more quantitative structural information may be derived from the β-hydrogen shifts. β-hydrogen spin densities obey the approximate relationship[22] $\rho_\beta^H = B\rho_N(\cos^2 \theta_\beta^H)$ and for freely rotating methyl groups $(\cos^2 \theta_\beta^H) = 0.5$. Thus, the ratio of the shifts $\Delta_\beta^H/\Delta_{CH_3}^H = 2\cos^2 \theta_\beta^H$ where θ_β^H is the dihedral angle between the nonbonding orbital and the bridgehead C-H bond. For compounds lacking the NCH_3 group we use the relationship $\rho_\alpha^H = A\rho_N$ where $B/A = 1.06 \pm 0.32$.[23] These equations lead to the dihedral angles and deviations from planarity at nitrogen, θ_N, given in Table II. An angle of ±55° for θ_N corresponds to a tetrahedral nitrogen and it is reassuring that all our angles are sensibly close to this value.

The vinyl hydrogen shifts in **5–10** are also of some interest with respect to the possible modes of spin delocalization to sites of unsaturation from the alternative orientations of the nitrogen lone pair. The positive shifts (α-spin densities in **5–7** are totally incompatible with direct delocalization of the unpaired electron into the π system VII:



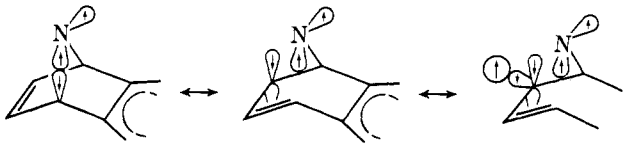
VII

for, although this process is allowed by the symmetries of the orbitals involved,[16,24] it would lead to β spin at the hydrogens in question:



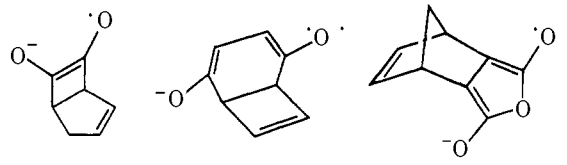
a requirement contrary to the observation.

These shifts could conceivably arise from the induction of β spin in the π cloud as the result of spin polarization of the N-C_1 and N-C_4 bonds accompanied by allyl delocalization into the double bond VIII



VIII

But, while this mechanism[17,26,27] evidently warrants serious consideration in for example IXa,[27] IXb,[26] and IXc,[17] we do



IXa IXb IXc

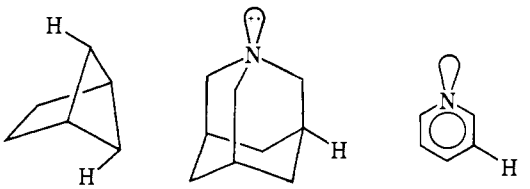
not favor such an explanation in the present case. There is no obvious reason why the same mechanism should not apply equally for the alternative orientation of the lone pair orbital, and yet it is found experimentally that inversion at nitrogen (**8** and **9**) leads to a reversal of the sign of the vinyl hydrogen spin densities. Furthermore these shifts are comparable in magnitude with those observed for the endo hydrogens in **1-4** and a simple vector analysis reveals that the angles between the lone pair orbital and the C-H bonds in question are comparable. Thus it is reasonable that there should be a practically equal contribution from homohyperconjugation in all the compounds **1-7** and it is unnecessary at this point to invoke any additional mode of spin delocalization.

In **8** and **9** where the nonbonding orbital is syn to the double bond, the vinyl hydrogens exhibit unusually large negative shifts, larger than for any of the comparable compounds **1-4** and **10** or for any of the model compounds. Apparently some additional mechanism is responsible for this increased β spin, and it seems most likely that with this arrangement of orbitals direct delocalization into the π system,[17,24,25,26] VII, does occur.

This proposal is subject to direct experimental test. As a result of α spin in the π orbitals, the olefinic carbons should exhibit larger positive shifts than would otherwise be expected by analogy with, for example, the saturated model. Moreover, methyl substitution on the double bond should result in a positive shift for the methyl protons, the magnitude of which should be comparable with those of the vinyl hydrogens in the presence of substantial π-orbital spin density but negligible in its absence.[17,25,26,27]

It is interesting that with this situation delocalization from the "front" lobe of the nonbonding orbital to the π bond appears to be of greater importance than from the "tail" lobe whereas many instances have been documented in which predominant delocalization takes place from a π orbital to the "tail" lobe of a C-H bond[6,17,27,29] or through a "tail-tail" interaction[7,18,30] as in X.

It therefore appears that, whereas the appropriate orientation of orbitals leads to bishomoconjugative *delocalization*,



Xa $J_{HH} = 7$ Hz[30a] Xb $a = 7.02$ G[30e] Xc $\Delta_R = 31°$[7]

the *stabilization* resulting from such delocalization is extremely small in comparison with other factors since in the present systems the replacement of the N-H bond by N-CH_3 leads to an apparent reversal of the invertomer populations.[13] This conclusion is also supported by the observation[2b,n] that 7-methyl substitution in the 7-norbornenyl radical substantially changes the syn to anti product distribution ratio. Caution should therefore be exercised in interpreting the stereochemistry of such systems in terms of homoconjugation alone.[2,17,27,31,37]

Experimental Section

NMR Measurements. All spectra were recorded on a Perkin-Elmer R20B spectrometer with a probe temperature of 35 °C. The proton resonance shifts were measured relative to internal TMS reference to eliminate bulk susceptibility shifts, and measurements were made using a Takeda-Riken TR-3824X frequency counter. Two methods were used for determining the contact shifts. For compounds **1-7** a solution of the amine in chloroform-*d* (ca. 1 M) was prepared, and its spectrum was recorded. To this were added increasing amounts of Ni(·acac)$_2$ and each time the spectrum was recorded. Relative shifts were obtained by plotting the chemical shifts against the Ni(acac)$_2$: amine ratio for at least six different concentrations. A linear least-squares regression analysis of the data provided a slope which was equated with the relative contact shifts, and hence the spin densities. The second method employed for compounds **8-10** shows linearity over the complete range of concentrations. This procedure involves the measurement of the chemical shifts of each proton in solutions at a constant Ni(acac)$_2$ concentration, but with different amine concentrations. The contact shift δ_{cs} for each proton in the various solutions is obtained by subtracting the measured chemical shift in the presence of Ni(acac)$_2$ from that obtained in the absence of Ni(acac)$_2$. The data can then be fitted to an equation of the form

$$[\text{amine}]_0 = [\text{Ni}]_0\Delta_{cs}\delta_{cs}^{-1} - K^{-1}$$

where $[\text{amine}]_0$ and $[\text{Ni}]_0$ are the total concentrations of the amine and of Ni(acac)$_2$, respectively, Δ_{cs} is the contact shift of the paramagnetic species produced, and K is the equilibrium constant for formation of the paramagnetic species.[32] For these measurements the Ni(acac)$_2$ concentration range was 0.03 to 0.04 M and the amine concentrations were varied from 0.1 to 2.0 M. At least six different concentrations were used for each amine. The best straight lines were obtained by a linear least-squares regression analysis. In all compounds where a direct comparison of these two procedures has been made the same relative spin densities were obtained.

Materials. Nickel bisacetylacetonate was purchased from Alfa Inorganics and was obtained in an anhydrous form by heating in vacuo at 61 °C for at least 15 h. Chloroform-*d* was obtained from Merck Sharp and Dohme of Canada Limited. Tetramethylsilane (TMS) was obtained from Stohler Isotope Chemicals.

Compounds 1,[33] **5,**[33] and **8**[34] have been reported previously. Compounds **6** and **7** were prepared by a method kindly furnished by Dr. Warrener.[35] A general procedure follows:

Anthranilic acid (0.40 mol) and isoamyl nitrite (0.058 mol) were added to a stirred solution of *N*-carbethoxypyrrole (0.058 mol) in refluxing dioxane and were stirred under reflux for an additional 15 min. The product was separated by chromatography over alumina. The product was not purified but was used directly in the next step. This carbamate (0.016 mol) in 10% aqueous NaOH was heated under reflux for 6 h after which period the desired product could be isolated and purified by distillation.

Compounds **2, 3,** and **10** were prepared by hydrogenation of the corresponding tetraene at 40 psi in 95% ethanol using a Pd/C catalyst.

For the preparation of **9**,[35] pentafluorobenzene (0.05 mol) in dry ether was reacted with *n*-butyllithium in the presence of *N*-methylpyrrole (0.15 mol) at −78 °C under an atmosphere of nitrogen followed by the usual work-up procedure.

Compound **4** was prepared by the reaction of tetrafluorobenzyne and *N*-benzylpyrrole[36] followed by hydrogenolysis-hydrogenation in methanol at 45 psi using 5% Pd/C catalyst with sufficient added concentrated HCl to make the solution acidic to litmus.

Physical and spectral properties were as follows.

2: mp 71-72.5 °C; NMR ($CDCl_3$) δ 6.87-7.08 (m, 3 H), 4.55-4.70 (m, 2 H), 2.30 (s, 3 H), 192-2.15 (m, 2 H), 1.10-1.40 (m, 2 H); IR ($CHCl_3$) 2990, 2950, 2870, 1600, 1460, 1340, 1060, and 810 cm^{-1}; mass spectrum *m/e* (rel. intensity) 159 (28), 158 (26), 157 (56), 156 (14), 142 (14), 141 (10), 132 (55), 131 (100), 130 (89), 129 (23), 128 (19), 115 (38), 103 (14), 77 (20), 65 (17). Anal. Calcd for $C_{11}H_{13}N$: C, 83.01; H, 8.17. Found: C, 82.82; H, 8.02.

3: bp 69-70 °C (0.5 mm); NMR ($CDCl_3$) δ 6.72-7.20 (m, 3 H), 4.45 (m, 2 H), 2.28 (s, 3 H), 2.25 (br s, 1 H), 1.9-2.1 (m, 2 H), 1.1-1.3 (m, 2 H); IR ($CHCl_3$) 2960, 2940, 2850, 1450, 1329, 1210, 910, 820 cm^{-1}; mass spectrum *m/e* (rel. intensity) 159 (2), 132 (18), 131 (100), 130 (24), 115 (5), 103 (4), 77 (4). Elemental composition was provided by high resolution mass spectrometry, 159.105. Found, 159.104.

4: bp 199-201 °C; NMR ($CDCl_3$) δ 4.80-4.95 (m, 2 H), 2.30 (br s, 1 H); 1.95-2.20 (m, 2 H), 1.10-1.40 (m, 2 H); IR ($CHCl_3$) 3300, 2960, 2820, 1500 cm^{-1}; mass spectrum *m/e* (rel. intensity) 217 (4), 216 (10), 202 (15), 200 (10), 190 (10), 189 (100), 152 (25). Elemental composition was provided by high resolution mass spectrometry, 217.051. Found, 217.050.

6: bp 68.5-70 °C (0.35 mm); NMR ($CDCl_3$) δ 7.00 (br s, 3 H), 6.71-6.81 (m, 2 h), 5.05 (br s, 1 H), 4.92 (br s, 1 H), 2.91 (br s, 1 H), 2.29 (s, 3 H); IR (neat) 3245, 3030, 2990, 1600, 1455, 1345, 1051 cm^{-1}; mass spectrum *m/e* (rel. intensity) 158 (14), 157 (100), 156 (33), 146 (44), 142 (58), 131 (72), 130 (67), 129 (47), 117 (31), 115 (58). Anal. Calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.01. Found: C, 84.25; H, 7.35.

7: bp 51-53 °C (0.03 mm); NMR ($CDCl_3$) δ 6.60-7.20 (m, 5 H), 4.89 (m, 2 H), 2.88 (s, 1 H), 2.25 (s, 3 H); IR ($CDCl_3$) 3000, 2910, 2850, 1600, 1450, 1350, 838, 810 cm^{-1}; mass spectrum *m/e* (rel. intensity) 157 (20), 142 (100), 141 (60), 98 (55), 71 (90), 67 (90), 44 (60), 43 (45).

9: mp 77-78 °C; NMR ($CDCl_3$) δ 6.91 (s, 2 H), 4.85 (m, 2 H), 2.15 (s, 3 H); IR ($CHCl_3$) 2975, 2950, 2860, 2780, 1480, 1370, 1290 cm^{-1}; mass spectrum *m/e* (rel. intensity) 231 (6), 230 (8), 216 (8), 204 (100), 203 (91), 202 (57), 201 (15), 200 (17), 188 (82), 187 (27), 169 (20), 162 (63), 161 (42), 151 (30), 143 (13), 102 (14). Anal. Calcd for $C_{11}H_9NF_4$: C, 57.14; H, 3.90. Found: C, 56.84; H, 4.06.

10: mp 33.5-35 °C; NMR ($CDCl_3$) δ 7.12 (s, 4 H), 4.05-4.20 (m, 2 H), 2.05-2.25 (m, 2 H), 2.04 (s, 3 H), 1.05-1.30 (m, 2 H); IR (neat) 3050, 2960, 2930, 2850, 2770, 1450, 1340, 1254, 755 cm^{-1}; mass spectrum *m/e* (rel. intensity) 159 (1), 158 (2), 157 (11), 156 (10), 132 (29), 131 (100), 130 (29), 128 (19), 116 (23), 115 (17), 9 (11). Elemental composition was provided by high resolution mass spectrometry, 159.105. Found, 159.105.

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(12) We choose this nonsystematic nomenclature and numbering in order to draw attention to the similarity between these amines and the 7-norbornenyl radical.

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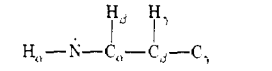

The values of the angles θ_β^C and θ_γ^H were calculated by vector analysis using carefully chosen bond lengths and bond angles and are rounded to the nearest 5°.

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Ion–Molecule Reactions of Simple Aliphatic Ketones by Continuous and Trapped ICR

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Abstract: It is shown that the ion-molecule chemistry of ketones is much more complicated than was assumed in previous papers. Double resonance acceleration of molecular ions even with rather low rf amplitudes leads to collision-induced dissociation. For ketones larger than acetone the molecular ion appears to isomerize. In addition to the well-known self-acylation reaction of molecular ions, solvated fragment ions are also formed by direct clustering of fragment ions with a neutral molecule. This leads to pressure-dependent double-resonance effects.

One of the well-known reactions in the ion-molecule chemistry of ketones is the formation of acylated product ions according to

$$RCOR^{\cdot+} + RCOR \rightarrow (RCOR)RCO^+ + R^{\cdot} \qquad (1)$$

This reaction appears to be characteristic of the keto form of the molecular ion and has been used in the structure elucidation of $C_3H_6O^+$ ions.[1] Bursey studied the acylation of a large number of molecules by the corresponding reaction of the molecular ion of diones and showed that the rate constant can be strongly dependent on stereochemical factors (see, e.g., ref 2 and 4). The rate constant of (1) for acetone has been reported by MacNeil and Futrell in an extensive study of the ion-molecule chemistry of this molecule.[5]

According to Tiedemann and Riveros[6] reaction 1 proceeds via an activated collision complex which for simple aliphatic ketones except acetone can be stabilized at pressures above 10^{-5} Torr:

$$\begin{array}{ccccc} RCOR^{\cdot+} + RCOR & \rightleftharpoons & (RCOR)_2^{\cdot+*} & \longrightarrow & (RCOR)RCO^+ + R^{\cdot} \\ & & \downarrow M & & \\ & & (RCOR)_2^{\cdot+} & & \end{array} \qquad (2)$$

These authors also studied the relative proton affinities of a large number of carbonyl compounds.[7]

In cooperation with Dr. J. van Thuijl of this laboratory and Professor A. Maquestiau of the University of Mons (Belgium) we have tried to use (1) in the structure determination of thioketone ions. The keto and enol forms of diisopropyl thioketone have different mass spectra and one should expect the molecular ions to have different structures.[8] With ICR we nevertheless found the $M = 217$ ion $(C_3H_7CSC_3H_7)C_3H_7CS^+$ in both cases. Subsequent double resonance experiments showed that the $M = 217$ ion was not formed from the molecular ion but by direct clustering of the $C_3H_7CS^+$ fragment ion with a neutral molecule. A comparable clustering of CH_3CO^+ with several neutrals has been reported by Bursey and co-workers (see, e.g., 3 and 4). We concluded that for a general case, reaction scheme 2 should at least be extended to:

$$\begin{array}{ccccc} RCOR^{\cdot+} + RCOR & \rightleftharpoons & (RCOR)_2^{\cdot+*} & \longrightarrow & (RCOR)RCO^+ \\ & & \downarrow M & & \uparrow M \\ & & (RCOR)_2^{\cdot+} & & (RCOR)RCO^{+*} \\ & & & & \updownarrow \\ & & & & RCO^+ + RCOR \end{array} \qquad (3)$$

It follows that the ion-molecule chemistry of aliphatic ketones is much more complicated than was assumed in previous papers. We therefore studied the reactions of ketone ions in more detail both with normal continuous and trapped ICR. As will be shown even reaction scheme 3 is too simple to account for all observations.

Experimental Section

All ICR results in this paper were obtained with a home-built instrument which includes a Varian 12-in. magnet and a diffusion-pumped vacuum system and dual inlet system constructed by VG Micromass. The solid-state marginal oscillator, built by Mr. J. D. van Gelder of this laboratory, was connected to either the reaction or the analyzer section of a flat four-section cell equipped with a four-grid electron gun. For normal ICR spectra, usually measured with grid modulation, the electronic detection system further consists of a PAR 122 lock-in amplifier, Keithley 610 CR electrometer, and Bryans 2-pens x-y recorder monitoring both the total ion current and the ICR signal intensity. Double resonance experiments were performed with either a Wavetek Model 112 or a Hewlett-Packard 4204A oscillator. The time evolution of ion intensities was measured with trapped ICR according to the method proposed by MacMahon and Beauchamp[9] using Tektronix 160 series pulse generators and a PAR 160 boxcar integrator. Frequencies and time delays were obtained from a Hewlett-Packard 6326A timer-counter. Pressures were read from a Vacuum Generators VIG-21 ion gauge located just outside the vacuum chamber.

Results and Discussion

Acetone. A continuous ICR spectrum of acetone at 1.2×10^{-5} Torr and the time evolution of ion intensities at 3×10^{-6}