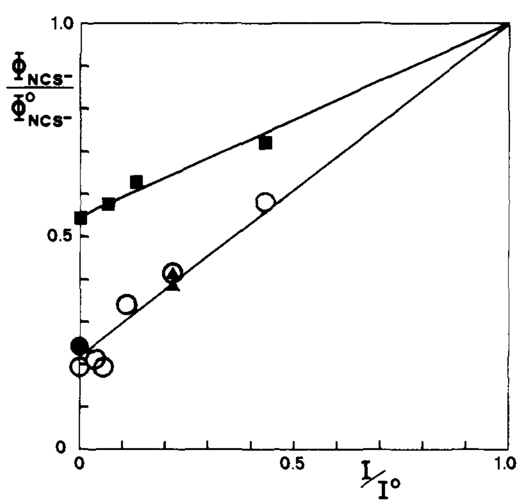

Figure 1. Plot of $\Phi_{NCS^-}/\Phi^0_{NCS^-}$ against I/I^0. The quenchers used were OH^- (■), $Ni(gly)_2$ (●), $Co(NH_3)_5Cl^{2+}$ (▲), and $Cr(CN)_6^{3-}$ (○).

the complex. A more reasonable mechanism seems that involving the formation of a seven-coordinate intermediate containing OH^- in the coordination sphere. Whatever the intimate mechanism of hydroxide quenching, our results show that the interaction between (^2E)- *trans*-$Cr(en)_2(NCS)_2^+$ and OH^- quenches the "intrinsic" manifestations (including phosphorescence emission and NCS^- aquation[20]) of the ^2E excited state, but introduces a new path for NCS^- aquation from ^2E. As there is no reason why this could not occur for other complexes,[21] the use of OH^- as a selective doublet quencher[5,9] in mechanistic studies of Cr(III) photochemistry should be avoided.[22,23]

Acknowledgment. Financial support from the National Research Council of Italy is gratefully appreciated.

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(20) By analogy with other Cr(III) complexes,[2,4,5,7–9] this reaction could take place from $^4T_2$ after $^2E \rightarrow {}^4T_2$ back-intersystem crossing.
(21) For $Cr(NH_3)_6^{3+}$, preliminary experiments with $Ni(gly)_2$ as a quencher have shown that the unquenchable part of the photoreaction is 50%; this value is noticeably lower than that obtained[5] by OH^- quenching (80–90%).
(22) For $Cr(phen)_3^{3+}$,[8] phosphorescence quenching by OH^- is accompanied by an *increase* in the quantum yield of the photoreaction. According to our mechanism, this result is expected when the new reaction path opened by the interaction between ^2E and OH^- is more efficient than the "intrinsic" ^2E reaction.
(23) For $Cr(en)_3^{3+}$, quenching by $CoCl_2$[7] and OH^- [9] seems to lead to approximately the same value for the fraction of unquenchable photoreaction. This means that in this case the interaction between ^2E and OH^- does not lead to an appreciable amount of photolysis products.

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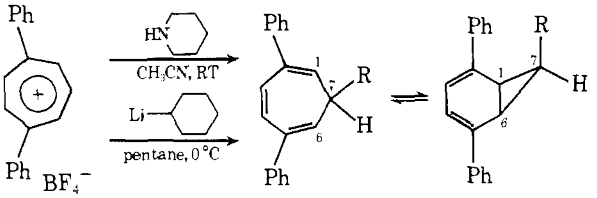
Effect of a C_7 π-Electron Donor on a Cycloheptatriene–Norcaradiene Equilibrium

Sir:

π-Electron donors in a bisected conformation at the C_7 (cyclopropyl) position are believed to destabilize norcaradienes either by weakening the C_1–C_6 bond through HOMO-LUMO interactions[1,2] or by repulsion between filled π-electron energy levels.[3] The validity of this theory not only bears on our understanding of cycloheptatriene and cyclopropane properties, but also on our fundamental understanding of resonance. We now report the first experimental evidence which demonstrates that replacement of hydrogen at C_7 with a π donor substituent can stabilize the norcaradiene form relative to the cycloheptatriene form and discuss possible explanations for this behavior.

Our approach has been to investigate the effect of a good donor group (the piperidino group) and the sterically equivalent[4,5] cyclohexyl group at C_7 on a closely balanced cycloheptatriene-norcaradiene equilibrium.[6,7] Pale yellow crystals (mp 120 °C dec, presumably **3a**)[8] were obtained in 94% yield on treatment of **1** with piperidine. Spectroscopic data indicated the rapidly equilibrating **2a** $\rightleftharpoons$ **3a** in solution: UV $\lambda_{max}^{CH_3CN}$ 273 (ϵ 21 400), 353 nm (8150); NMR (CCl_4, 25 °C) δ 7.24 (m, 10 H, phenyl), 6.76 (s, 2 H, $H_{3,4}$), 4.45 (d, 2 H, $H_{1,6}$, $J_{17} = 4.8$ Hz), 2.72 (m, 4 H, NCH_2), 1.80 (t, H_7, $J_{17} = 4.8$ Hz), and 1.57 (m, methylene) (the latter two m 7 H together). Treatment of **1** with cyclohexyllithium afforded **2b** $\rightleftharpoons$ **3b** in 8% yield. The latter were separated from their 7-cyclohexyl-1,5-diphenylcycloheptatriene (mp 143–144 °C) and 7-cyclohexyl-1,4-diphenylcycloheptatriene isomers, each formed in 17% yield, by elution with pentane on neutral alumina and on 40% silver nitrate on silica gel followed by selective crystallization from pentane–ether–methanol: white crystals; mp 123–125 °C (presumably **3b**);[8] UV λ_{max}^{hexane} 241 (ϵ 37 100), 322 nm (8750); NMR (CS_2, 25 °C) δ 7.25 (10 H, phenyl), 6.92 (s, 2 H, H_3 and H_4), 4.75 (d, 2 H, H_1 and H_6, $J_{17} = J_{67} = 5.5$ Hz), and 0.5–2.3 (m, 12 H, H_7 and cyclohexyl). In CCl_4 at 25 °C $H_{1,6}$ absorb at δ 4.88.

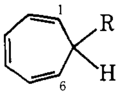


1 **2** **3**

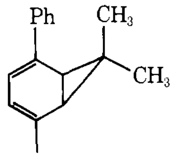
a, R = 1-piperidino
b, R = cyclohexyl
c, R = H

The time-averaged values of $\delta_{H_{1,6}}$ in **2a** $\rightleftharpoons$ **3a** (4.45) and **2b** $\rightleftharpoons$ **3b** (4.88) indicate that, in contrast to **2c** (5.74),[6,7] substantial quantities of the norcaradiene form are present in both mixtures. The equilibrium constants (K) can be calculated if the value of $\delta_{H_{1,6}}$ in each valence isomer is known.[9] Normally $\delta_{H_{1,6}}$ (CHT) $-\delta_{H_{1,6}}$ (NOR) is 2.2-3.0 ppm. However, these data could not be obtained by the usual low temperature NMR studies; in vinyl chloride the **2a** $\rightleftharpoons$ **3a** solution froze at −165 °C and **2b** $\rightleftharpoons$ **3b** precipitated at −93 °C before the individual isomers could be observed.

Nevertheless, the required chemical shifts could be satisfactorily estimated as follows. As increasing amounts of trifluoroacetic acid are added to **2a** $\rightleftharpoons$ **3a** in D_2CCl_2 at 25 °C, the $H_{1,6}$ doublet at δ 4.46 shifts downfield until it reaches a maximum value of ca. δ 6.0 on addition of 1.0 mol equiv.[10] At this point the equilibrium has completely shifted to the 7-(1-piperidinium) salt corresponding to **2a.** Since $\delta_{H_{1,6}}$ of the model compound **4a**[11] in $DCCl_3$ shifts from 5.50 to 5.72 on protonation by 1 mol equiv of trifluoroacetic acid, it can be estimated that $\delta_{H_{1,6}}$ for **2a** is 5.8. The same value for $\delta_{H_{1,6}}$ of **2a** is obtained from $\delta_{H_{1,6}}$ (**2c**) + $\delta_{H_{1,6}}$ (**4a**) − $\delta_{H_{1,6}}$ (**4c**) (all in CCl_4) or 5.74 + 5.36 − 5.28 = 5.82. Similarly, $\delta_{H_{1,6}}$ (**2b**) is estimated to be $\delta_{H_{1,6}}$ (**2c**) + $\delta_{H_{1,6}}$ (**4b**)[12] − $\delta_{H_{1,6}}$ (**4c**) = 5.6. Finally, values for $\delta_{H_{1,6}}$ (**3a**) (2.5) and $\delta_{H_{1,6}}$ (**3b**) (2.6) were estimated from $\delta_{H_{1,6}}$ (**5**)[13,14] (2.38) and the chemical shifts of analogous substituted cyclopropanes.[15]



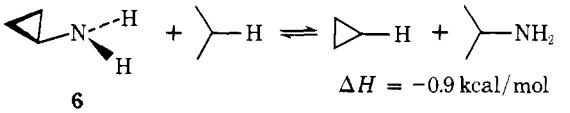
4a, R = 1-piperidino
b, R = cyclohexyl
c, R = H



5

From these data one obtains $K_{25\,°C}$ (**2a** $\rightleftharpoons$ **3a**) ≈ 0.7 (41% **3a**) and $K_{25\,°C}$ (**2b** $\rightleftharpoons$ **3b**) ≈ 0.3 (24% **3b**). Essentially the same value for $K_{25\,°C}$ (**2a** $\rightleftharpoons$ **3a**) is obtained from the values of J_{17} in **2a** $\rightleftharpoons$ **3a,** (vide supra) and in **4a** (5.5 Hz), and from J_{12} (trans) in cyclopropylamine (3.6 Hz).[15c] This is consistent with the expectation that the piperidino and cyclohexyl groups occupy the less hindered pseudoequatorial positions in both **2a** $\rightleftharpoons$ **3a** and **2b** $\rightleftharpoons$ **3b.**[16] It also clearly establishes that a piperidino group stabilizes the norcaradiene form (relative to the cycloheptatriene form) slightly more than does the sterically similar[4,5] cyclohexyl group. Since replacement of hydrogen at C_7 with alkyl groups strongly shifts the equilibrium toward the norcaradiene form (cf. **2c** ($K_{25\,°C} < 0.1$) and **5**), we conclude that replacement of a hydrogen at C_7 with a piperidino group causes a >1 kcal/mol relative stabilization of the norcaradiene form.

These results contrast with the few published data available. Heat of combustion data suggest that the isodesmic reaction in eq 1 is *exothermic* by 0.9 kcal/mol.[17] Note that the perpendicular conformation of cyclopropylamine (**6**) has been shown[18,19] and calculated[20,21] to be more stable than the bisected conformation (**7**). NMR data demonstrate that **8** is the favored tautomer[22] in its equilibrium with **9.** Furthermore, it can be estimated from the behavior of **8** $\rightleftharpoons$ **9** on protonation (the signal for H_a moves *upfield*)[22] and from expected values for δ_{H_c} and δ_{H_o} in **8** and **9** (based on dihydrobullvalene as a model)[23] that $K_{25\,°C}$ (**8** $\rightleftharpoons$ **9**) ≈ 0.1-0.2. (The position of this equilibrium is probably not steric in origin since recent results with substituted methylenebarbaralanes[24] suggest that interaction of the N-benzyl group with an adjacent hydrogen would, if anything, favor **9.**) This value is consistent with the expectation[8,9,20,21] that the cyclopropylamino group in the perpendicular conformation, as suggested by models for **3a,** is more stabilizing electronically than one in the bisected conformation, as in **9.**



(1)

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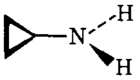

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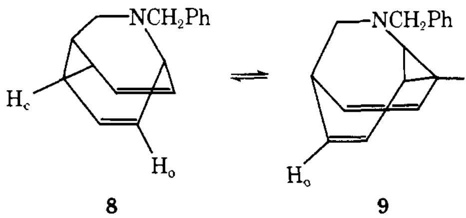

8 **9**

How can these facts be explained? One possibility is that π interactions play a role. HOMO-LUMO interactions always cause a lowering of the occupied orbital and thus lead to stabilization. Thus, contrary to the published model,[1,2] *HOMO-LUMO interactions between π-electron donors and a cyclopropyl ring, whether in a perpendicular or a bisected conformation, must cause stabilization, not destabilization.* Effects on one bond (e.g., the C_1–C_6 bond) do not necessarily reflect those on the molecule as a whole. By this model, protonation of the amino group would localize the nitrogen lone pair and decrease this interaction.

However, the role of σ binding energies must also be considered. It is expected that the electronegative ammonium group would shift the equilibrium toward the cycloheptatriene side (protonated **2a**).[25] Recent results suggest that the cyclohexyl group in **2b** and the piperidino group in **2a** seemingly have comparable σ-bond effects.[26] In view of the small effects involved, we are not yet able to assess the relative roles of σ and π effects. However, we can conclude that replacement of a hydrogen at C_7 by an amino group can cause a significant relative stabilization of the norcaradiene form.

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(10) The values of molar equivalents of trifluoroacetic acid, $\delta_{H_{1,6}}$ (ppm), and J_{17} (Hz) were 0.0, 4.45, ~4.6; 0.2, 4.82, 5.0; 0.5, 5.34, 5.7; 1.0, 6.02, 6.0; 2.0, 5.98, 6.0, respectively. Smaller downfield shifts are observed if methanol is added instead.
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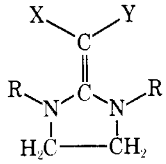
Demonstration of Fourfold Rotational Barriers in Push-Pull Ethylenes

Sir:

The barrier to rotation around the carbon-carbon double bond in ethylenes with strong donor groups on one carbon atom and strong acceptors on the other may be quite low owing to a superior stabilization of the zwitterionic transition state.[1-3] When this effect is combined with a strong steric interaction between the donor and acceptor groups, permanently twisted ethylenes result.[4,5] An example is found in **1**, where a free-energy barrier to passage through the planar state of 16.9 kcal/mol has been evaluated by bandshape analysis of the AB spectrum of the benzylic protons.[6] The x-ray crystallographic structure of **2**[5] shows nearly planar CO-C-CN and imidazolidine parts with a dihedral angle between these planes of 41°. For these molecules the relation between the potential energy and the dihedral angle (θ) may have a high "steric barrier" at $\theta = 0$ and 180° and a lower barrier caused by loss of π-electron interaction across the double bond (the π-electron barrier)[4] at 90 and 270°. It is evident that the steric as well as the π-electron barrier have important contributions from both kinds of energy.



1, X = PhCO; Y = $COCH_3$; R = CH_2Ph
2, X = p-BrC_6H_4CO; Y = CN; R = CH_3
3, X = Ph; Y = CN; R = CH_2Ph
4, X = Ph; Y = CN; R = CH_3
5, X = p-$NO_2C_6H_4$; Y = CN; R = CH_2Ph

The benzylic protons in compounds like **1** with strong acceptor groups show only one AB spectrum down to −140 °C, *i.e.*, their π-electron barriers are too low to be measured. In **3** on the other hand, the benzylic proton resonance shows no AB spectrum in the accessible temperature region but only a symmetrical doublet below −94 °C, showing that the π-electron barrier is 8.5 kcal/mol but that the steric barrier is too low to be measured. In **4** the π-electron barrier is 9.5 kcal/mol,[7] and the barrier difference between this molecule and **3** is probably due to increased ground-state strain caused by the benzyl groups. In **5**, the nitro group lowers the π-electron barrier and only a singlet benzylic proton resonance is observed above −140 °C.

In **6**, the increased ring size raises the steric barrier, and it can be measured by DNMR technique. An AB spectrum appears below −54 °C, corresponding to a steric barrier of 10.7 kcal/mol. Below −90 °C first the high-field part and then also the low-field part of the AB spectrum undergo selective broadening. At −130 °C new very broad signals have emerged, and at this and higher temperatures the spectrum can be satisfactorily simulated by use of the DNMR-3 program,[8] assuming exchange between two AB systems.[9] From the rate constants a π-electron barrier of 7.0 kcal/mol can be derived. An analogous barrier in **7** gives rise to a decoalescence of the

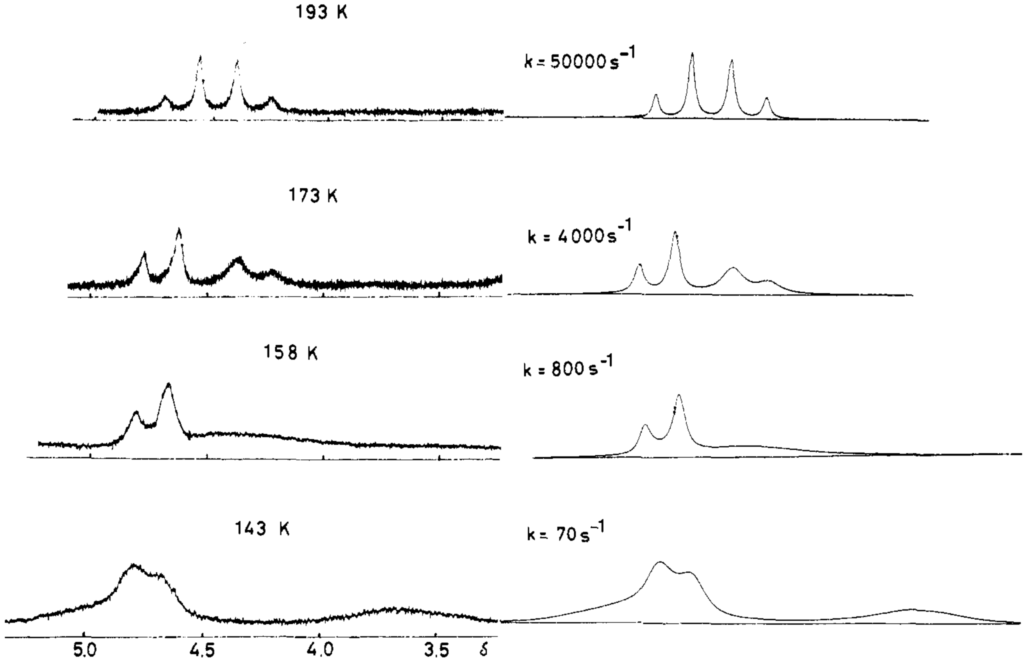


Figure 1. Experimental (100 MHz) and calculated spectra of the benzylic methylene protons of **6**. Chemical shifts: A_1, δ 4.67; A_2, δ 4.58; B_1, δ 3.57; B_2, δ 4.94. T_2 (from top to bottom): 0.10, 0.07, 0.05 and 0.03 s.