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DEUTERIUM ISOTOPE EFFECT IN C.d. of KETONES -
EXPERIMENT AND THEORY

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The recently reported dissignate β-equatorial deuterium isotope effect on a c.d. of ketones 1[1] and 2[2] prompts us to report our related study on α-axial and γ-deuterium isotope effects in compounds 3, 4 and 5[3]. Compounds 3 and 4 were synthesized straightforwardly from the corresponding alkenes by epoxidation with m-Cl perbenzoic acid, followed by reduction with $LiAlD_4$ and subsequent oxidation of the corresponding alcohols with Jones's reagent. The deuterium in 3 and 4 was then removed by both acid and base catalysis; the c.d. spectra of the deuterated and exchanged ketones were recorded under identical conditions in EtOH. The results, uncorrected for isotopic purity (determined by mass spectrometry), are presented under the structures.

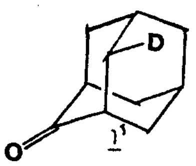
The data for 1 to 5 shows that the substitution of D for H in a coupling path[4] results in a dissignate contribution as would be expected if D were a net σ-electron withdrawer. This behaviour is identical, but weaker, to that of similarly oriented $NR_3^{\oplus}$ group[4] or F[1,5] (a weak π-donor but a strong σ-acceptor) and contrasts well with the strong consignate effect of σ-donors such as $SnMe_3$ group in 6[6] and 7[7].

In order to verify this conclusion, we have carried out CNDO/2 calculations [8] on a model pentanone-2, 8, and a cyclohexanone, 9, in which we varied the electronegativity of the starred terminal Me, α-ax, β-ax and β-eq hydrogen atoms * and studied the twists of the n and π^* orbitals on oxygen. Using the relationship,

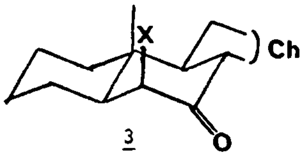
$$\delta R \sim -\delta\Theta \quad \text{[9]} \quad \text{where}$$

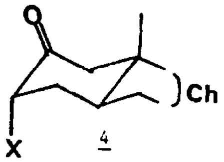
$$\Theta = \Theta_n - \Theta_{\pi^*} \quad \text{and} \quad \delta\Theta = \Theta_{\text{subst. ketone}} - \Theta_{\text{parent ketone}}$$

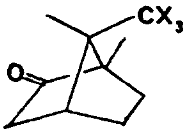
it can be seen in Figure 1 that a substitution of H by D on a coupling path (α-ax, β-eq - Figure 1.b.) and γ - Figure 1.a)) should result in a dissignate $\delta\Delta\varepsilon$ if D is <u>more electronegative</u> than H. However, β-ax D (noncoupling path) should show a consignate effect[9] - Figure 1.b). The comparison of Figures 1.b) and 1.c) shows the importance of Θ_{π^*} contribution to Θ for $H_{\alpha ax}$ specially at larger electronegativities than normal.

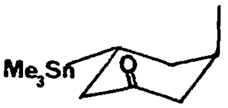

1[1]
$\Delta\varepsilon$ + ·082 (isopen.)

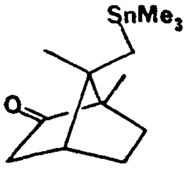

2[2]
$\Delta\varepsilon$ + ·014 (EPA)

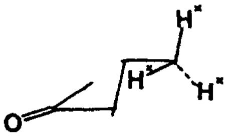

3
X = H $\Delta\varepsilon$ -·77
D $\Delta\varepsilon$ -·88 (94% D)

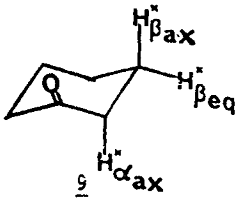

4
X = H $\Delta\varepsilon$ + 2·41
D $\Delta\varepsilon$ + 2·26 (95% D)


5[5]
X = H $\Delta\varepsilon$ + 1·50
= D $\Delta\varepsilon$ + 1·36


6
$\Delta\varepsilon$ + 6·51


7
$\Delta\varepsilon$ + 10·1


8


9

The same dissignate deuterium isotope effect can also be reproduced by the shortening of the C—H bond length, albeit to a much lesser extent for any realistic bond shortening. It is probable that the experimental result is a combination of both the electronegativity and bond length changes.

*The electronagativity change of an H atom was affected by altering its $\frac{1}{2}(I_\mu + A_\mu)$ term in the equation for its diagonal element of the Fock matrix ($F_{\mu\mu}$).

The greater electronegativity of D relative to H is also borne out by other studies such as the solvolytic kinetic effects [10] or photoelectron spectroscopy.[11] All these effects concern essentially the energy of the occupied levels. Where disagreement occurs, it is when the unoccupied levels are also considered.

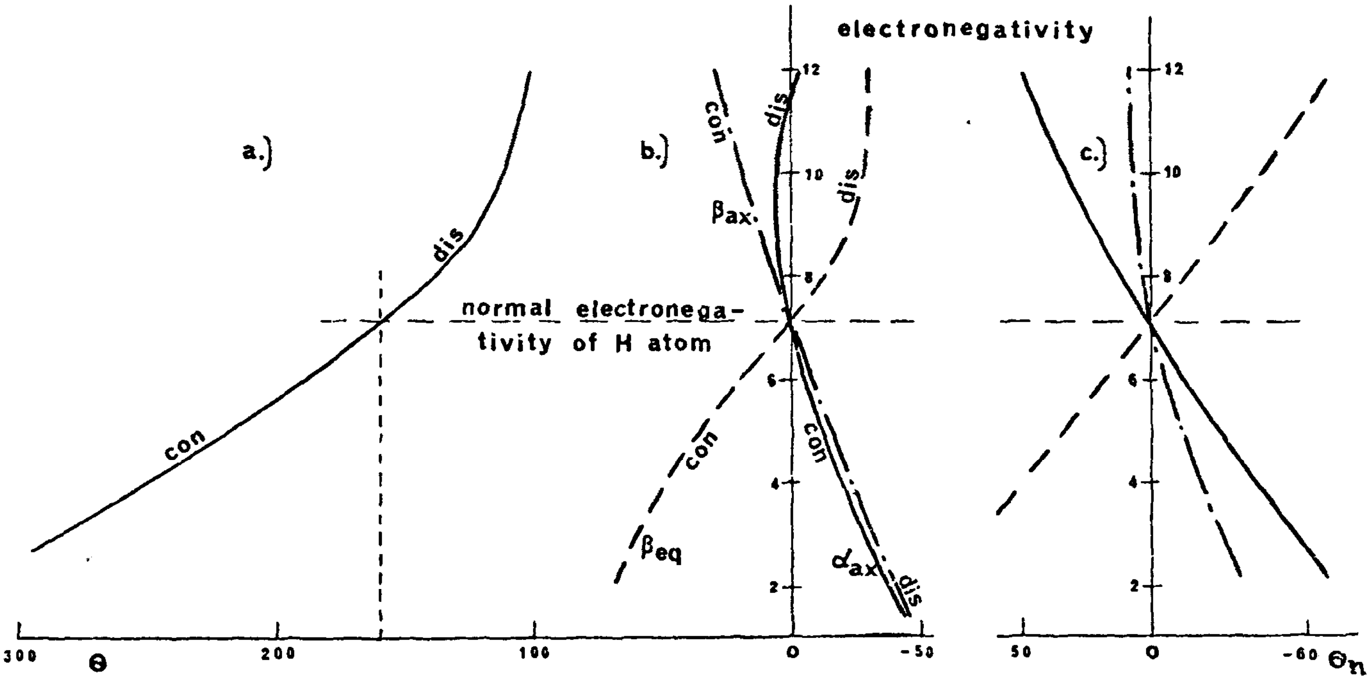


FIGURE 1

Variation of Θ(Θ_n) with electronegativity change of starred H atoms in
a.) pentan-2-one, 8 ; b.) and c.) cyclohexanone, 9 (see text).
Con = consignate and dis = dissignate contribution to the c.d.

These, and our earlier[9], calculations show that the oxygen orbital twist, Θ[9], a Frontier Orbital property, is proportional both in sign and relative magnitude to the electric transition moment of the $n \longrightarrow \pi^*$ transition which in turn controls the sign and the magnitude of the Cotton effect[9,12](as the magnetic transition moment is virtually constant). It is a resultant of the summation of local electric transition moments situated on each atom of a molecule[13]. These arise in molecules such as 2 simply from the fact that the substituent, D, and its mirror image atom, $H_{\beta_{eq}}$, mix unequally the n_y and π_x manifolds delocalised over the whole molecule and thus result in small, but important changes, in the symmetry of the HOMO and LUMO orbitals[9].

REFERENCES

1. D.A. Lightner, T.C. Chang and J.Horwitz, Tetrahedron Lett., 3019 (1977).
2. C. Djerassi, C.L. Van Antwerp and P. Sundararaman, Tetrahedron Lett., 535 (1978).
3. W.L.Meyer, A.P. Lobo and R.N. McCarty, J.Org.Chem., 32, 1754 (1967).
4. J. Hudec, Chem.Comm., 829 (1970).
5. G. Snatzke and G. Eckhart, Tetrahedron, 24, 4543 (1968); ibid., 26, 1143 (1970).
6. J. Hudec, J.Chem.Soc., Perkin I., 1020 (1975).
7. Unpublished work.
8. J. Pople and G.A. Segal, J.Chem.Phys., 44, 3289 (1966).
9. E.E. Ernstbrunner, M.R. Giddings and J. Hudec, Chem.Comm., 953, 954, 956 (1976).
10. M. Tarle, S. Borcic and D.E. Sunko, J.Org.Chem., 40, 2949 (1975).
11. V.H. Dibeler, R.M. Reese and M. Krauss, Adv.Mass Spectrometry, 3, 471 (1966); A.J.C. Nicholson, J.Chem. Phys., 43, 1171 (1965).
12. Y.H. Pao and D.P. Santry, J.Amer.Chem.Soc., 88, 4157 (1966); T.D. Bowman and D.A. Lightner, J.Amer.Chem.Soc., 96, 3145 (1976).
13. M.R. Giddings and E.E. Ernstbrunner, J.Chem. Soc. Perkin II, in press.