

have been expected to produce IV exclusively if IV were truly significantly more stable, suggested that a determination of the equilibration of IV and V under acid catalysis be made. The study of the equilibration was complicated somewhat by the fact that both IV and V rearrange to 4-isopropyl-*o*-xylene (VI), whose identity was proved by oxidation¹¹ to 3,4-xylic acid, m.p. 164–165°. The pseudo-first order rate constant for conversion of either IV or V to VI in 0.25 *M* toluenesulfonic acid in acetic acid at 25.0° was 1.1×10^{-4} sec.⁻¹. Simultaneous with the production of VI, the isomers IV and V approach an equilibrium in which the ratio of IV:V is about 9. During the early stages of the isomerization (the first half-life), the ratio IV:V can be determined quite accurately and has reached the values of 88:12 (starting from 96% pure V) and 92:8 (starting from 97% pure IV). Unfortunately the v.p.c. analytical method becomes highly inaccurate as the substances IV and V become minor components of the reaction mixture, so the further approach to equilibrium cannot be observed.

When the ΔF for $V \rightleftharpoons IV$ is calculated using $K = 9$, a value of -1.3 kcal./mole results. This measurement of an equilibrium between two compounds of a common skeleton and degree of hydrogenation at once eliminates the problems involved in the choice of model compounds for use in calculation of resonance energies from heats of hydrogenation data. Since 1,6-overlap is clearly impossible in V, it follows that the stabilization of IV over V, in the absence of other effects, will measure directly the stabilization effected by 1,6-overlap.

It is clear, however, that IV is stabilized relative to V to some extent in that the olefinic bond involved in the isomerization is trisubstituted in IV and only disubstituted in V. On the other hand, Dreiding models indicate that the strain energy involved in making the triene system in IV coplanar is larger than that involved in making the triene coplanar in V, since in this latter case the triene system can approximate coplanarity even though the seven-membered ring remains strongly puckered at the 1 and 7 positions. (The λ_{max} of V at higher wave length than that of IV probably reflects this.) It is difficult to assess the relative importance of these two opposing effects, so that one cannot decide in which direction, or by how much, it is necessary to modify the experimentally determined value of 1.3 kcal./mole stabilization of tropilidene by 1,6-overlap.¹² Nevertheless, it is clear that 1,6-overlap is by no means the major factor in this system that it has been postulated to be.

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RECEIVED MAY 22, 1961

(11) O. Kruber, *Ber.*, **57**, 1008 (1924).

(12) If one makes the *prima facie* reasonable assumption that a measure of the stabilization of IV over V due to strain and degree of substitution will be given by that of methylcycloheptene over methyl-encycloheptane, with amounts to 2.3 kcal./mole,¹³ it follows that 1,6-overlap is actually *destabilizing* by 1.0 kcal./mole. It is evident that this extreme assumption is unjustified.

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LONG-RANGE PROTON SPIN-SPIN INTERACTIONS: THE ¹³CH₃ SATELLITES IN ACETONE

Sir:

Several examples of resolvable nuclear magnetic resonance absorption lines arising from the coupling between protons separated by four or more bonds recently have been reported.^{1,2,3} We have observed such a coupling in acetone which, we believe, arises from a coupling mechanism different from those operating in the previously analyzed systems. The acetone coupling depends upon a mechanism related to the one recently proposed by Karplus⁴ for unsaturated systems but different in that the unsaturated bond is not a link in the connective bond chain between the protons.

The proton resonance spectrum⁵ of acetone consists of a single sharp line, which arises from the six equivalent methyl protons, surrounded symmetrically by two weak satellite groups at ± 63.6 cps., which arise as a result of the ¹³C–H coupling in the 2.2 mole per cent. of acetone molecules containing one ¹³CH₃ group. Under high resolution the ¹³CH₃ groups each split into a well-resolved 1:3:3:1 quadruplet with a spacing of 0.54 ± 0.05 cps. This quadruplet is the result of long-range spin-spin coupling of the ¹³CH₃ protons to the non-equivalent ¹²CH₃ protons four sigma bonds away. This spacing is equal to the coupling constant A_{HH} between protons on the two methyl groups.

A coupling of similar magnitude was observed in acetoxime, (CH₃)₂C=NOH, in saturated tetrahydroethylene solution; however, the solution was relatively dilute and accurate measurements were not feasible because of an unfavorable signal-to-noise ratio. On the other hand, the ¹³CH₃ satellites of the related alcohol (CH₃)₂CHOH show no evidence of an appreciable coupling between the methyl groups. We estimate a value of A_{HH} not greater than 0.2 cps., based on the observed line widths.

Previous examples of resolvable long-range proton-proton coupling through sigma-bonded systems¹ have involved compounds in which there are fixed or highly favored conformations of the molecules with respect to rotation about the carbon-carbon bonds through which the protons interact. This is to be expected in view of the dependence of the magnitude of coupling constants on the dihedral angle between bonding orbitals on adjacent carbon atoms.⁶ In acetone, however, the internal rotation frequency about the carbon-carbon bonds is very much greater than the proton resonance frequencies used, the barrier to rotation being approximately 2.8 kcal./mole. Furthermore, the C–C–C bond angle differs from 120° by not more

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(2) J. N. Shoolery, L. Johnson and W. A. Anderson, *J. Mol. Spectroscopy*, **5**, 110 (1960).

(3) (a) E. B. Whipple, J. H. Goldstein and W. E. Stewart, *J. Am. Chem. Soc.*, **81**, 4761 (1959); (b) E. B. Whipple, J. H. Goldstein and L. Mandell, *J. Chem. Phys.*, **30**, 1109 (1959).

(4) M. Karplus, *J. Am. Chem. Soc.*, **82**, 4431 (1960); *J. Chem. Phys.*, **33**, 1842 (1960).

(5) All spectra were observed at 40 Mc. with a Varian Associates Model V4300-B high resolution n.m.r. spectrometer. Frequency measurements were made by the sideband method using a calibrated Hewlett-Packard Model 200D audiofrequency oscillator.

(6) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959).

than a few tenths of a degree,⁷ so ordinary sigma-electron contributions to the observed coupling would be expected to be very small.⁸

Karplus⁴ has shown that anomalously large spin-spin interactions between protons on carbon atoms which are separated by one or more pi bonds may be explained by including contributions from low-lying ³Π states and σ-π interactions⁹ in the C-H bonds. He related the proton-proton coupling constant to the isotropic electron-proton splitting constants for the pi-radical fragments corresponding to the ³Π states and the excitation energies for the (¹Π → ³Π) transitions.

We wish to point out that such ³Π states would be expected to contribute significantly to proton-proton coupling through sigma systems which are geminal to an unsaturated bond, as in acetone or in ethylene.

The coupling constant A_{HH} may be expressed as

$$A_{HaHb} = K \sum_n \frac{\langle \Psi_0 | \mathcal{H}_a | \Psi_n^T \rangle \langle \Psi_n^T | \mathcal{H}_b | \Psi_0 \rangle}{E_0 - E_n} \quad (1)$$

in the notation used by Karplus.⁴ We assume that the only excited state of importance in the calculation of the pi electron contribution to the coupling is the triplet $(CH_3)_2C^{\cdot}O^{\cdot}$ and we estimate an excitation energy $\Delta\pi$ of about 6.3 eV.^{10,11} We use a simple valence bond approach and write the ground state Ψ_0 and the triplet state Ψ_0^T functions as

$$\begin{aligned} \Psi_0 &= \eta \psi_{\text{covalent}} + \sqrt{1 - \eta^2} \psi_{\text{ionic}} \\ &= \left\{ \eta \left[\frac{C(1)O(2) + O(1)C(2)}{\sqrt{2}} \right] + \sqrt{1 - \eta^2} [O(1)O(2)] \right\} \\ &\quad \left[\frac{\alpha(1)\beta(2) - \beta(1)\alpha(2)}{\sqrt{2}} \right] \end{aligned} \quad (2)$$

and

$$\Psi_0^T = \left[\frac{C(1)O(2) - O(1)C(2)}{\sqrt{2}} \right] \left[\frac{\alpha(1)\beta(2) + \beta(1)\alpha(2)}{\sqrt{2}} \right] \quad (3)$$

where C and O are $2p_z$ atomic orbitals of carbon and oxygen, respectively, α and β represent electronic spin states with $m_s = +1/2$ and $-1/2$, respectively, and $1 - \eta^2$ is the ionic character of the bond. Overlap integrals of the form $\langle C | O \rangle$ are neglected. We can separate the acetone triplet into the fragments $(CH_3)_2C^{\cdot}$ and O^{\cdot} , and neglect the contribution from the latter. Both groups of protons then couple with the same pi electron. The coupling constant a_H for a H_3C-C^{\cdot} fragment is known from e.s.r. measurements.^{5,10} With these wave functions and an approach similar to that of Karplus,⁴ we obtain

$$A_{HH}(\pi) \cong -k\eta^2(a_H)^2/\Delta\pi \quad (4)$$

where k has the same numerical value as in Karplus' expression. This result implies that the pi contribution to the coupling is negative in sign and is related to the long-range methyl-methyl coupling observed in the 2-butene system by the expression

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$$A_{HH}(\text{acetone}) = -\eta^2 \frac{\Delta\pi_{C=C}}{\Delta\pi_{C=O}} A_{HH}(\text{2-butene}) \quad (5)$$

The observed value of $A_{HH}(\text{2-butene})$ is about 1.2 cps.¹² and $\Delta\pi_{C=C}$ has been estimated⁵ to be about 6.0 eV. Values of $A_{HH}(\text{acetone})$ and $\Delta\pi_{C=O}$ have been indicated above. These figures when inserted into Eq. 5 yield an ionic character $1 - \eta^2$ of 0.53, in reasonable agreement with the range 0.42 to 0.52 given by Pauling¹³ for the ionic character of the C=O bond. The explanation for the coupling in acetoxime is similar.

In acetone the negative value of A_{HH} arises because the two groups of protons are both coupled directly to the same unpaired electron which orients the proton spins parallel to each other.

It is of interest to point out that this treatment predicts a pi contribution of about -1.5 cps. to the *gem* proton-proton coupling in the vinyl group and in ethylene (assuming $\Delta\pi = 6.0$ eV.) in addition to the sigma contribution of +3.1 cps. estimated by Gutowsky, Karplus and Grant⁸ for a 120° H-C-H bond angle. It seems probable that this effect can account for the fact that observed values of $A_{HH}(\text{gem})$ (1 to 2 cps.) in these systems are smaller than previously calculated values by small but significantly consistent amounts.

The long-range proton-proton interactions observed by Roberts¹ in methacrolein dimer and by Fraenkel¹⁴ in methyl formate also may be due in part to enhanced coupling from the C=O groups in these molecules.

It is a pleasure to acknowledge financial support in the form of a grant from the Research Corporation under which this work was carried out.

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RECEIVED MAY 31, 1961

A NEW SYNTHESIS OF α - ω -DINITROALKANES

Sir:

We wish to report a new ring opening reaction of mono-potassium α, α' -dinitrocyclanones (I) which provides a highly convenient route for the preparation of α, ω -dinitroalkanes.

Hitherto, the only methods which have been available for preparing α, ω -dinitroalkanes were the Victor Meyer reaction¹ and a modification of this reaction.^{2,3}

The new synthesis involves the alkaline nitration⁴ of the readily available C₅-C₇ cyclic ketones, the *in situ* conversion with glacial acetic acid of the resulting dipotassium α, α' -dinitrocyclanones to I and the hydrolytic cleavage of the latter to α, ω -dinitroalkanes.

Nitration of cyclopentanone⁴ and acidification of the reaction mixture at 10° with glacial acetic acid gave 88% of Ia ($n = 2$). Acidification of Ia

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