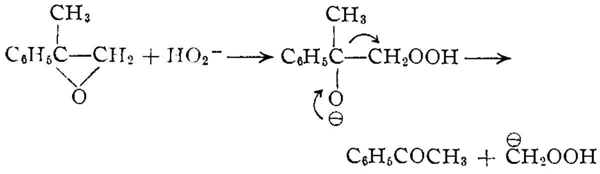
react with alkaline hydrogen peroxide in 90% methanol at room temperature gives an almost quantitative yield of acetophenone. The product obtained is most readily explained by the equation



α-Methylstyrene (b.p. 164–165°, n^{20}D 1.5384) was treated with N-bromosuccinimide and water to obtain the bromohydrin; α-methylstyrene oxide was then obtained by the action of aqueous sodium hydroxide on the bromohydrin.[2] Careful distillation of the product gave epoxide with the following properties: b.p. 84.5–85.5° (17 mm.), n^{20}D 1.5208 (lit.[3] b.p. 85° (17 mm.)), n^{20}D 1.5208. Calcd. for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.78; H, 7.29.

To 25 ml. of 90% methanol, 0.5 *N* in potassium hydroxide, was added 0.24 g. of epoxide and 5 ml. of 30% hydrogen peroxide. At the end of 48 hours an 85–90% yield of acetophenone was isolated as the 2,4-dinitrophenylhydrazone (m.p. and mixed m.p. 247–248°; lit.[4] m.p. 247–248°). Similar experiments were carried out in which potassium hydroxide and then hydrogen peroxide were eliminated from the reaction medium. In either case little if any acetophenone was produced.

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(2) C. O. Guss and R. Rosenthal, THIS JOURNAL, **77**, 2549 (1955).

(3) R. Rothstein and J. Ficini, *Compt. rend.*, **234**, 1694 (1952).

(4) G. D. Johnson, THIS JOURNAL, **75**, 2720 (1953).

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RECEIVED OCTOBER 26, 1956

INTRAMOLECULAR VAN DER WAALS–LONDON COHESIONS IN BUTADIENE AND BENZENE

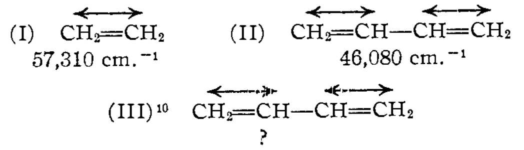
Sir:

The idea of (localized) electrons in neighboring bonds within a molecule oscillating in phase with each other has been put forward repeatedly in connection with the electronic spectra of compounds containing conjugated double bonds.[1,2,3] London's explanation of van der Waals attraction between molecules[4] is based on a similar idea, *viz.*, the interaction between oscillating molecular dipoles. In the simplest possible model, two identical spherically symmetrical molecules, a distance R apart, each having a dipole oscillation of frequency ν_0 and a corresponding polarizability α, interaction produces six modes of oscillation, one in-phase and one out-of-phase along each axis, of frequencies $\nu = \nu_0\sqrt{1 \pm q}$, where $q_{\text{par.}} = 2\alpha/R^3$, $q_{\text{perp.}} = \alpha/R^3$. The zero-point stabilization energy of the two interacting units, relative to the two isolated units (expanded to terms in q^4), is

$$U_0 = {}^1/_2 h\Sigma\nu - 6 \times {}^1/_2 h\nu_0 \doteqdot -{}^3/_4 h\nu_0(\alpha^2/R^6 + \alpha^4/R^{12})$$

Similar interactions between identical bonds (or electron pairs) within a molecule, and weaker ones between dissimilar units, affect molecular properties ranging from chemical reactivities[5] to diamagnetic susceptibilities; these interactions are especially prominent if the molecule contains (highly polarizable) π-electrons and account for many effects conventionally explained by π-electron delocalization.[6]

Quantitative estimates of van der Waals–London cohesions based on the above approach[7] are possible only for systems possessing a high degree of regularity, such as polyenes. Butadiene is comparable with two ethylene molecules, benzene (assumed to have the Kékulé structure[8]) with three. The main cohesion energy, due to interaction of the logitudinal π-electron oscillations,[9] $U_{0(\text{longit.})}$, is best obtained by evaluating q, the "effective" $2\alpha/R^3$, from spectrally observed absorption frequencies. The appropriate modes of oscillation and the spectral frequencies assigned to them are roughly[6] as shown in (I) to (VI). The frequencies of (II) and (III), and similarly those of (V) and (VI), are approximately related to the ethylene frequency ν_0 as $\nu_0\sqrt{1 - q}$ and $\nu_0\sqrt{1 + q}$.



(I) $CH_2{=}CH_2$
57,310 cm.$^{-1}$

(II) $CH_2{=}CH{-}CH{=}CH_2$
46,080 cm.$^{-1}$

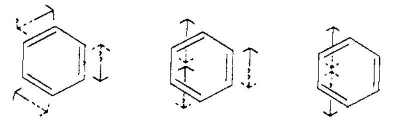
(III)[10] $CH_2{=}CH{-}CH{=}CH_2$
?

For butadiene

$$U_{0(\text{longit.})}{}^{11} \doteqdot -{}^1/_2 hc \times 57{,}310 \times {}^1/_4\left[1 - \left(\frac{46080}{57310}\right)^2\right]^2 \doteqdot -2.7 \text{ kcal./mole}$$

this is considerably less than the cohesion energy obtained by Simpson's[12] wave-mechanical approach (5.5 kcal./mole).[6]

(IV)[10] (V) (VI)[10](?)



[13]38,460 cm.$^{-1}$ 50,000 cm.$^{-1}$?

For benzene

$$U_{0(\text{longit.})}{}^{11} \doteqdot -{}^1/_2 hc\left[(57310 - 38460) + 57310 \times {}^1/_4 \left\{1 - \left(\frac{50000}{57310}\right)^2\right\}^2\right] = -28 \text{ kcal./mole}$$

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(1) D. Radulescu, *Ber.*, **64**, 2223 (1931).

(2) G. N. Lewis and M. Calvin, *Chem. Revs.*, **25**, 273 (1939).

(3) W. Kuhn, *Helv. Chim. Acta*, **31**, 1780 (1948).

(4) F. London, *Trans. Far. Soc.*, **33**, 8 (1937), and references cited there.

(5) E. Spinner, *J. Chem. Soc.*, 1590 (1956).

(6) See E. Spinner, forthcoming publication, for detailed discussion.

(7) K. S. Pitzer and E. Catalano have just treated the paraffins successfully by a different approach (THIS JOURNAL, **78**, 4844 (1956)).

(8) For criticism of the concept of π-electron delocalization see A. Burawoy, "Contribution a l'Étude de la Structure Moleculaire," Desoer, Liege, 1948, p. 73, and references cited there.

(9) Other coördinated electron oscillations produce additional stabilizations.

(10) Transition forbidden.

(11) Accurate to terms in q^2.

(12) W. T. Simpson, THIS JOURNAL, **73**, 5363 (1951).

(13) A. Burawoy, *et al.*, attribute this band to a transition involving an electron migration around the ring (*J. Chem. Soc.*, 3721 (1955)).

this represents the greater part of the stabilization conventionally attributed to π-electron delocalization.

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RELATIVE REACTIVITIES OF TOLUENE, TOLUENE-α,α,α-d_3 AND TOLUENE-α-t IN ELECTROPHILIC NITRATION, MERCURATION AND BROMINATION[1]

Sir:

We have found that secondary isotope effects on the rate of nuclear aromatic nitration, mercuration and bromination due to isotopic substitution for hydrogen in the methyl group are 3% per deuterium atom or less. The larger (4–30% per deuterium) secondary isotope effects previously observed in solvolysis have been interpreted in terms of hyperconjugation in the transition state.[2] Therefore either hyperconjugation is relatively less important in these aromatic substitutions than in the solvolyses (including p-$CH_3{}^*C_6H_4CHClCH_3$ in acetic acid at 50°) or the reported p-methyl isotope effects in solvolysis are not measuring hyperconjugation. In view of the extreme importance of other kinds of resonance in aromatic substitution (*e.g.*, relative rates of about $10^{18}:10^9:1$ for bromination of aniline, anisole and benzene[3]) it is unexpected that hyperconjugation should be so minor. Therefore we favor the latter interpretation.

Summarizing our experimental results: Toluene-α,α,α-d_3 (2.7 D) and toluene-α-t were prepared by reduction of α,α,α-trichlorotoluene with zinc and acetic acid-d or -t.[4] The molar activity of toluene-α-t recovered after 92% reaction with nitronium ion (0.5 M toluene plus 10 M nitric acid containing 20% water by volume) at 25° was 0.86 ± 0.77% higher than that of the starting material (scintillation counting) corresponding to an isotope effect of 1.003 ± 0.003 for k_H/k_T or 1.002 ± 0.002 for k_H/k_D per deuterium atom. There was no exchange of methyl hydrogens under these nitration conditions, since the nitrotoluenes produced had the same molar activity as the starting material within 2.8 ± 3.5% (ionization chamber counting).

Mercuration of toluene-α,α,α-d_3 by Hg^{++} (0.2 M toluene plus 0.05 M mercuric acetate in acetic acid solution containing 0.25 M water and 0.50 M perchloric acid) at 25° gave an isotope effect of 1.00 ± 0.03 per deuterium (determined by direct rate comparison rather than by competition experiment). Under mercuration conditions, toluene-α-t did exchange tritium slowly with the solvent, but the exchange reached less than 5% completion during the time of the mercuration kinetics.

In bromination of toluene-α-t by Br_2 (0.05 M reactants in 85% acetic acid–15% water solution) at 25° the molar activity of toluene recovered after 81% reaction showed a 7.7 ± 1.4% increase, corresponding to an isotope effect of 1.046 ± 0.009 for k_H/k_T or 1.03 ± 0.01 for k_H/k_D per deuterium atom. Bromotoluenes from complete bromination had the same molar activity as the toluene within experimental error (± 3%).

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RECEIVED OCTOBER 1, 1956

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[1] The bromination work was supported by the Office of Naval Research under Contract No. N5ori-07838 (*cf.* T. E. C. K., Ph.D. thesis, M. I. T., Sept., 1956, for complete experimental data) and subsequent mercuration and nitration work (by A. J. K.) by the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the United States Government.

[2] E. S. Lewis and C. E. Boozer, THIS JOURNAL, **74**, 6306 (1952); **76**, 791, 794 (1954); V. J. Shiner, Jr., *ibid.*, **75**, 2925 (1953); **76**, 1603 (1954); **78**, 2653 (1956); E. S. Lewis and G. M. Coppinger, *ibid.*, **76**, 4495 (1954); E. S. Lewis and R. R. Johnson, Abstracts of Papers presented at 130th Meeting of the American Chemical Soc., Atlantic City, New Jersey, Sept. 16 to 21, 1956, p. 20-O; A. Streitweiser, R. H. Jagow and S. Suzuki, THIS JOURNAL, **77**, 6713 (1955).

[3] P. W. Robertson, P. B. D. de la Mare and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953).

[4] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **34**, 98 (1956).

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syn-7-NORBORNENYL TOLUENESULFONATE[1]

Sir:

As reported recently,[2] *anti*-7-norbornenyl p-toluenesulfonate (IV) is more reactive than the related 7-norbornyl derivative (VI) in acetolysis by a factor of 10^{11}, the anchimerically assisted ionization leading to cation (VII). We now report the preparation of the previously unavailable isomeric *syn*-7-norbornenol (III) and the novel solvolytic behavior of its toluenesulfonate (V).

From opening of bicycloheptene oxide (I) with hydrogen bromide, there is obtained predominantly the Wagner–Meerwein rearranged bromohydrin (II), m.p. 75–76°. By the action of potassium t-butoxide in benzene on the toluenesulfonate of the bromohydrin (II), there is obtained *syn*-7-norbornenyl toluenesulfonate (V), m.p. 67–68°, in *ca.* 80% yield. Hydrogenation of this material leads to the known 7-norbornyl derivative (VI). Analogous treatment of the tetrahydropyranyl derivative of the bromohydrin II with potassium t-butoxide and hydrolysis led to *syn*-7-norbornenol (III), m.p. of phenylurethan 125–126°, m.p. of p-toluenesulfonate 67–68°.

First order rate constants of acetolysis of the *syn*-toluenesulfonate (V) are (1.17 ± 0.02) $\times 10^{-6}$ sec.$^{-1}$ at 100.0° and (1.28 ± 0.01) $\times 10^{-5}$ sec.$^{-1}$ at 122.2°, leading to an extrapolated value of 2.6 $\times 10^{-11}$ sec.$^{-1}$ at 25°. While the *syn*-material (V) is slower than its *anti*-isomer (IV) by a factor of 10^7, it is nevertheless anchimerically accelerated, since it is more reactive than the 7-norbornyl ester (VI) by a factor of 10^4. The source of the anchimeric assistance is clear from the nature of the solvolysis product from (V).

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[1] (a) Research sponsored by the Office of Ordnance Research, U. S. Army; (b) supported in part by the Petroleum Research Fund of the American Chemical Society.

[2] (a) S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, THIS JOURNAL, **77**, 4183 (1955); (b) S. Winstein and M. Shatavsky, *ibid.*, **78**, 592 (1956); (c) C. J. Norton, Thesis, Harvard University, 1955.