A NON-CONJUGATED 1,3-DIENE

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1. RECENT interest[1] in the properties of o-di-t-butylbenze-
nes prompts us to report the remarkable spectral properties
of an acyclic system, 2,3-di-t-butyl-1,3-butadiene[2] (I). Its
structure, proven adequately by ozonization experiments[2] was
confirmed by examination of its NMR spectrum (one singlet at
$\mathcal{T}$ = 8.9, and two symmetrical doublets (each with J = 1.5
cps) at $\mathcal{T}$ = 4.9 and $\mathcal{T}$ = 5.3; relative areas 18 : 2 : 2). The
ultraviolet absorption spectrum (fig. I) of the vapor[4] taken
at room temperature under nitrogen shows the absence of the

[1] A.W. Burgstahler and M.O. Abdel-Rahman, J. Amer. Chem. Soc.
85, 173 (1963) and references cited therein.

[2] H.J. Backer, Rec. trav. chim. 58, 643 (1939).

[3] NMR spectra were measured on a Varian A-60 instrument.
Chemical shifts for the spectra (in CCl_4) are relative to
tetramethylsilane as internal standard.

[4] Taken on a Cary model 14, with the kind cooperation of
Prof. Kommandeur and the Department of Physical Chemistry
of this University.

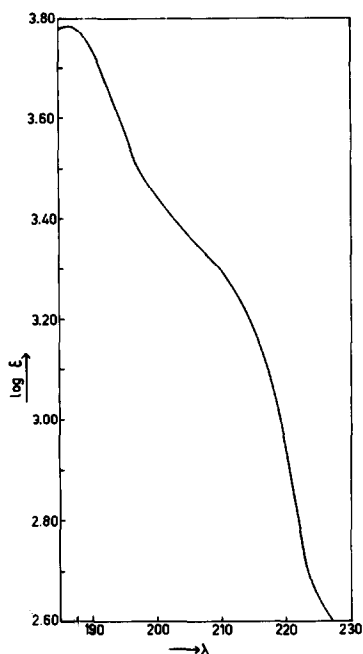[*] Department of Structural Chemistry.

Fig. I. Spectrum of 2,3-di-
t-butylbutadiene (vapor)

typical dialkyldiene absorption maximum at 220 mμ (vapor)[5,6] ± 5 mμ. Instead the spectrum of I shows a maximum near 185 mμ and a shoulder at 209 mμ which is characteristic of a substituted ethylene.[5] Molecular models strikingly show that the two coplanar conformations[7] normally assigned to butadienes, namely the trans (IIa) and cis (IIb) are sterically unlikely for this diene. An orthogonal conformation, termed skew by us, is clearly the favored one (IIc). A number of intriguing questions are raised by the existence of a stable non-conjugated 1,3-diene. Whether the

[5] S.F. Mason, Quart. Rev. 15, 287 (1961) for recent data and literature references on absorption spectra of olefins and dienes.

[6] L.C. Jones and L.W. Taylor, Anal. Chem. 27, 228 (1955).

[7] W.J. Bailey and H.R. Golden, J. Amer. Chem. Soc. 75, 4780 (1953) and A.T. Blomquist and D.T. Longone, ibid. 79, 3916 (1957) have observed an abnormally low (220 mμ) maximum for 1,2-dimethylenecyclohexane, the latter authors commenting on the deviation from coplanarity of the chromophore.

$$CH_2 = C(C(CH_3)_3) - C(C(CH_3)_3) = CH_2$$

I
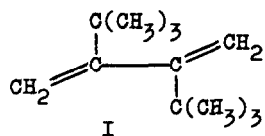
Newman, classical and orbital projections of butadienes

IIa
trans

IIb
cis

IIc
skew
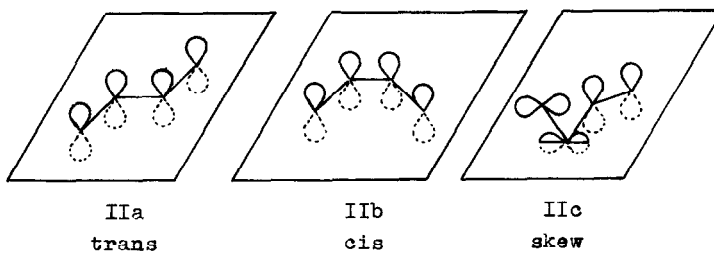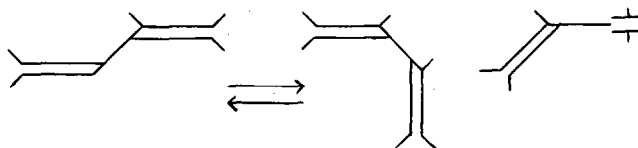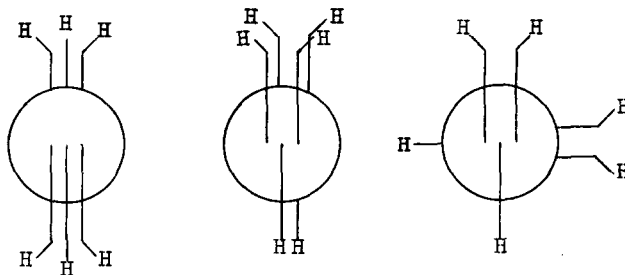
C_2-C_3 bond length in butadienes is a function of pi-orbital overlap or of sp^2 hybridization[8] and what other physical and chemical properties[9] are affected in this and related[10] systems must await further study.

2. Calculations of the electronic spectrum (D.W. Davies).

The object of this section is to discuss the relation between the electronic spectrum and conformation of butadienes.

There has been much theoretical work on cis- and trans-butadiene,[11] but a theoretical treatment of the skew con-

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[8] a. M.J.S. Dewar and H.N. Schmeising in "Conference on Hyperconjugation", Pergamon Press, 1959, p.83;
b. A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists", J. Wiley and Sons, N.Y., 1962, p.166. The near orthogonality of the double bonds in cyclo-octatetraene represents an interesting analogy to our acyclic system.

[9] Preliminary studies in this laboratory (lack of diene chemical reactivity, viz. polymerization) support the concept.

[10] N.J. Leonard and P.M. Mader, J. Amer. Chem. Soc. 72, 5388 (1952) studied the angle of twist about the inter-carbonyl bond of α - diketones and assigned an angle e of 90-180° to dipivaloyl. An important difference between the latter chromophore and (I) lies in the presence of the 4-vinyl hydrogen in the butadiene, forcing this molecule in to the skew conformation. For a discussion of conjugation, coplanarity and reactivity in diphenyls see P.B.D. De la Mare and J.H. Ridd in "aromatic Substitution", Butterworths, London, 1959, p.157 and ref. 8.b, p.242.

[11] J. Fain and F.A. Matsen, J. Chem. Phys. 26, 376 (1957), and references quoted there.

formation does not seem to have been given. A similar con-
formation, however, occurs in cyclo8ctatetraene which can
be regarded as two coupled _skew_ butadienes. The electronic
spectrum of cyclo8ctatetraene has been successfully treated
by Schiess and Pullman,[12] who used the molecular orbital
method due to Pariser and Parr.[13] A simple treatment of
cis- and _trans_-butadiene, also based on Pariser and Parr's
method, has been given by Longuet-Higgins and Murrell.[14]
They treated the butadienes as interacting ethylene mole-
cules, obtaining the energies of the transitions in the bu-
tadienes from the experimental value for the "local energy"
transition in the ethylene system. They also considered con-
figurations in which the electrons are transferred from one
double bond to the other.

Their method is applied here to butadiene and 2,3-disub-
stituted butadienes in the _trans_- and _skew_-conformations.
Butadiene is regarded as two methylethylene systems, and
the substituted butadienes as two gem disubstituted systems.
For the local energies, the values of the N-V transitions in
methylethylene (7.19 eV), and 2-methylpropene (6.59 eV) were
used. Longuet-Higgins and Murrell[14] suggested that ethylene
should be taken as the local system for butadiene, but they
used for the local energy the value 7.06 eV, which is more
appropriate for a substituted ethylene. Other values needed
for the calculations are the resonance and electron repulsi-

[12] P. Schiess and A. Pullman, _J. Chim. Phys._ _53_, 101 (1956).

[13] R. Pariser and R.G. Parr, _J. Chem. Phys._ _21_, 466, 767
(1953).

[14] H.C. Longuet-Higgins and J.N. Murrell, _Proc. Phys. Soc._
A, _68_, 601 (1955).

on integrals between the ith and jth atoms, β_{ij} and γ_{ij}
respectively. For γ_{ij}, i and j not adjacent, the inverse dis-
tance approximation[15] was used. The bond lengths[16] were
taken as C=C 1.337 Å and C-C 1.483 Å and the angles as 120°.
In the trans-butadiene values for γ_{12}, β_{12}, and β_{23} were
taken from Pariser and Parr,[13] and the value for γ_{23} from
Schiess and Pullman.[12] For the skew butadiene β_{23} was taken
as 0.4 times the value in the trans-butadiene. Calculations
were also made for β_{23} = 0. The parameters used are shown
in table 1.

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Table 1

Resonance and electron repulsion integrals (eV)

integral	12	13	14	23
γ trans	7.38	5.89	3.94	6.71
skew			4.41	
β trans	-2.92			-1.68
skew	-2.92			-0.67

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The results obtained for the two lowest transitions of buta-
diene and of 2,3-disubstituted butadienes are shown in table
2. The experimentally observed decrease in the energy differ-
ence between the two lowest transitions when substituents
are introduced is reproduced in the calculations, and the
overall agreement is satisfactory. The inclusion of substitu-
ent effects by changing the local energy value seems to be
justified.

    The calculations show that there should be a hypsochromic

[15] J.A. Pople, Trans. Faraday Soc. 49, 1375 (1953).

[16] A. Almenningen, O. Bastiansen and M. Traetteberg,
Acta Chem. Scand. 12, 1221 (1958).

shift in going from a _trans_- to a _skew_-butadiene, and they
support the view expressed above that 2,3-di-_t_-butylbuta-
diene has a _skew_ conformation.

Table 2

Energies (eV) and wavelengths (mµ) of lowest transitions

system	β_{23}	energy theory	wavelength	
			theory	expt.[5]
trans-butadiene	-1.68	6.98	178	173
		6.35	195	207
2,3-disubstituted	-1.68	6.38	194	193[a]
trans-butadienes		6.04	205	220
2,3-disubstituted	-0.67	6.54	190	186[b]
skew-butadienes		6.32	196	(209)[c]
	0	6.92	179	
		6.26	198	
hypsochromic			theory	expt.
shift			4, 9	7, 11
[a] 2,3-dimethylbutadiene [b] this work [c] shoulder				