values obtained from the data of substituted methanes are directly related to J_{CH} of substituted aldehydes, XCHO. A plot of J_{CH}(XCHO) *versus* ζ_x is a straight line with a slope = 4.01 and an intercept = 5.3, as determined by a method of least squares. Consequently, any J_{CH} of the substituted aldehydes can be predicted from the equation

$$J_{CH}(\text{XCHO}) = 5.3 + 4.01\,\zeta_x \qquad (2)$$

Calculated and experimental coupling constants of various substituted aldehydes, along with corresponding zeta values, are presented in Table I.

TABLE I

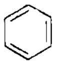
CALCULATED AND OBSERVED C^{13}-H COUPLING CONSTANTS OF SUBSTITUTED ALDEHYDES

Substituent	ζ,[a] cps.	J_{CH}, cps., calcd.	J_{CH},[e] cps., exptl.	Diff.
–H	41.7	172.5	172[3]	−0.5
$-C(CH_3)_3$	40.6	168.1	168.6	−0.5
$-CH(CH_3)_2$	39.0[b]	161.7	168.9	+7.2
$-CH_2CH_3$	41.0[c]	169.7	170.6	+0.9
$-CH_3$	42.6	176.1	172.4	−3.7
$-C_6H_5$	42.6	176.1	173.7	−2.4
–*p*-C_6H_4Cl	42.9	177.3	175.2	−2.1
–*m*-C_6H_4Cl	43.4	179.3	177.5	−1.8
–*o*-C_6H_4Cl	44.1	182.1	182.8	+0.7
$-CCl_3$	50.6	208.2	207.2	−1.0
$-N(CH_3)_2$	47.6	196.2	191.2	−5.0
$-OCH_3$	54.6[4]	224.2	226.2	+2.0
$-OCH_2CH_3$	53.4[d]	219.4	225.6	+6.2
–F	65.6	268.4	267[5]	−1.4

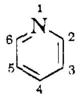
[a] Calculated from data for methyl derivatives except where indicated otherwise, see ref. 1. [b] Calculated from $J_{CH}((CH_3)_2CH\mathbf{CH_2}Cl)$ = 147.3 cps. [c] Calculated from $J_{CH}(CH_3CH_2\mathbf{CH_2}Cl)$ = 149.3 cps. [d] Calculated from $J_{CH}(CH_3\mathbf{CH_2})_2O)$ = 137.7 cps. [e] From proton spectra using a Varian Associates DP-60 Spectrometer.

We believe the additivity rule can be accounted for if overlap integrals are retained in calculations based on the Fermi contact term.[6] The ζ values determined from the methanes appear in eq. 2 for the aldehydes because the overlap integrals are essentially, at least to our approximation, independent of the state of hybridization of the carbon atoms. The coefficients in eq. 2 arise because of the difference in the state of hybridization of the carbon atom in the methanes, sp^3, as compared to its hybridization in the aldehydes, sp^2. Previous investigators[7,8] have shown that J_{CH} depends upon the state of hybridization of the carbon atom; similar arguments are held to be true here. Obviously since the carbonyl oxygen is common to all aldehydes its contribution to the coupling must be essentially a constant and, therefore, an additivity relation analogous to eq. 1 must be expected for the aldehydes.

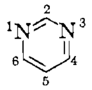
Benzene (I), pyridine (II) and pyrimidine (III) represent a series of compounds which also contain sp^2 carbon atoms. Table II shows very clearly that this series does obey the additivity relation. For convenience in notation the coupling components are expressed as ζ_{ij}', where the prime indicates that the carbon orbital is sp^2 rather than sp^3 and the subscripts ij indicate only the first and second atoms of the substituent group. For example, consider the C–H bond in the 2 position in pyridine. N_1 is α and C_6 is β to the C_2–H bond, so we write ζ_{NC}' for the component of this group. Again C_3 is α and C_4 is β to the C_2–H bond, so we write ζ_{CC}' for the component of this group. In this series it is not necessary to define the substituent group beyond the β position because of the negligible effect of any atom further removed. From the available data self-consistent ζ' values have been assigned and are listed in Table II. This table clearly shows that these values well account for the data and, thereby, illustrates the extensibility of the additivity rule for substituents on C^{13}–H coupling for carbon in its various states of hybridization.



I



II



III

TABLE II

CALCULATED AND OBSERVED C^{13}-H COUPLING CONSTANTS OF BENZENE, PYRIDINE AND PYRIMIDINE, USING ζ'_{CC} = 77.5 CPS., ζ'_{CN} = 84.5 CPS. AND ζ'_{NC} = 103.0 CPS.

C–H bond	J_{CH}, calcd.	J_{CH}, exptl.	Diff.
Benzene	$\zeta'_{CC} + \zeta'_{CC} = 155.0$	158	−3.0
2, pyridine	$\zeta'_{CC} + \zeta'_{NC} = 180.5$	179	+1.5
3, pyridine	$\zeta'_{CC} + \zeta'_{CN} = 162.0$	163	−1.0
4, pyridine	$\zeta'_{CC} + \zeta'_{CC} = 155.0$	152	+3.0
2, pyrimidine	$\zeta'_{NC} + \zeta'_{NC} = 206.0$	206.0[9]	0
4, pyrimidine	$\zeta'_{CC} + \zeta'_{NC} = 180.5$	181.8[9]	−1.3
5, pyrimidine	$\zeta'_{CN} + \zeta'_{CN} = 169.0$	168.0[9]	+1.0

Further work along these lines is being conducted in this laboratory.

[3] P. C. Lauterbur, *J. Chem. Phys.*, **26**, 217 (1957).

[4] H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1961).

[5] N. Muller, *ibid.*, **36**, 359 (1962).

[6] N. F. Ramsey, *Phys. Rev.*, **91**, 303 (1953).

[7] J. N. Shoolery, *J. Chem. Phys.*, **31**, 1427 (1959).

[8] N. Muller and D. E. Pritchard, *ibid.*, **31**, 768, 1471 (1959).

[9] G. S. Reddy, R. T. Hobgood, Jr., and J. H. Goldstein, *J. Am. Chem. Soc.*, **84**, 336 (1962).

[10] National Defense Fellow (Department of Health, Education, and Welfare).

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RECEIVED MAY 11, 1962

NEW LOWER LIMIT FOR THE BINDING ENERGY OF THE HELIUM MOLECULE ION[1]

Sir:

The literature contains three *experimental* values for the binding energy[2] of He_2^+. D_e = 3.1 e.v. obtained[3] by an extrapolation of the Rydberg spectrum of He_2, $D_e \geq 1.4$ e.v. from[4] electron impact experiments and D_e = 2.16 e.v. from[5] the analysis of scattering data.

[1] This research was supported by the Robert A. Welch Foundation of Houston, Texas, and Air Force Office of Scientific Research.

[2] The zero-point energy ~0.2 e.v. has been neglected in this discussion.

[3] G. Herzberg, "Spectra of Diatomic Molecules," Molecular Spectra and Structure, D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950, Second Edition, Vol. I, p. 536.

[4] J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951).

[5] E. A. Mason and J. T. Vanderslice, *J. Chem., Phys.*, **29**, 361 (1958).

Quantum mechanical calculations have now progressed to the point where they can set useful lower bounds to binding energy in simple systems. That is, by the variation principle D_e (exp.) $\geq E_{\text{atoms}}$ (exp.) $-$ E_{molecule}(calcd.). We accordingly have carried out an *ab initio* calculation using a $^2\Sigma_u{}^+$ *valence-bond* function with the terms $(1s_a 1s_a{}' 1s_b{}'')$, $(1s_a{}'' 2s_a 1s_b{}'')$, $(1s_a 2s_a 1s_b{}'')$, $(1s_a 1s_a{}' 2s_a)$, $(1s_a 1s_a{}' 2p_{oa})$, $(2s_a{}^2 1s_b{}'')$, $(2p_{oa}{}^2 1s_b{}')$, $(2p_{\pm 1a} 1s_b{}'')$, $(3p^2{}_{oa} 1s_b{}'')$, $(3p_{\pm 1a} 1s_b{}'')$, $(3d_{oa}{}^2 1s_b{}'')$, $(3d_{\pm 1a} 1s_b{}'')$, $(3d_{\pm 2a} 1s_b{}'')$ $(1s_a 2p_{oa} 1s_b{}'')$, $(1s_a{}'' 3p_{oa}{}'' 1s_b{}'')$ $(1s_a{}'' 3d_{oa} 1s''{}_b{}'')$, $(2s_a 2p_{oa} 1s_b{}'')$, $(2s_a 3p_{oa} 1s'')$, $(2p_{oa} 3p_{oa} 1s_b{}'')$ $(1s_a{}'' 3s_a 1s_b{}'')$, $(3s_a{}^2 1s_b{}'')$. Slater orbitals have been used and the primes indicate different orbital exponents on the same orbitals.

The results are listed in Table I together with the results of previous investigations. It is clear that we have eliminated the lower bound of 1.4 e.v. obtained by Hornbeck and Molnar[4] and replaced it by the theoretical lower bound[10] of 2.045 e.v. Details of this calculation will be reported in a later publication.

TABLE I

Author	D_e(e.v.)
Pauling,[6] 1st	no binding
Pauling, 2nd	0.05
Weinbaum[7]	0.7
Moiseiwitsch,[8] 1st	no binding
Moiseiwitsch, 2nd	0.65
Moiseiwitsch, 3rd	0.76
Csavinszky[9]	0.84
Present calculation[10]	2.045

(6) L. Pauling, *J. Chem. Phys.*, **1**, 56 (1933).

(7) S. Weinbaum, *ibid.*, **3**, 547 (1935).

(8) B. L. Moiseiwitsch, *Proc. Phys. Soc.* (London), **A69**, 653 (1956).

(9) P. Csavinszky, *J. Chem. Phys.*, **31**, 178 (1959).

(10) NOTE ADDED TO PROOF.—With a slightly larger wave function, we have found a new lower bound of 2.14 e.v.

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RECEIVED MAY 11, 1962

MOLECULAR STRUCTURE, DIPOLE MOMENT, AND QUADRUPOLE COUPLING CONSTANTS OF DIAZIRINE

Sir:

It is now a well established fact that diazomethane and aliphatic diazo compounds do not have the cyclic three-membered ring structure that originally was proposed by early workers in the field of nitrogen chemistry. Recently this same three-membered ring structure has been assigned to a newly discovered class of compounds, diazirine and substituted diazirines.[1,2,3] We have measured the rotational spectrum of diazirine and wish to report that analysis of our data decisively proves the cyclic assignment to be correct.

The sample used in this work was kindly provided by Dr. W. H. Graham.[4] Measurements were made in the frequency region 7.8 to 41 kMc. with a Stark-modulation type microwave spectrometer which has been described previously.[5] Using the Stark effect as a guide, twelve very strong absorptions were assigned as "A" type transitions of the common isotopic species of diazirine in its ground vibrational state. The Stark effect also provided the basis for assignment of eight weaker absorptions to rotational transitions of $H_2{}^{13}CN_2$ (1.1% in natural abundance) and $H_2C^{14}N^{15}N$ (0.7% in natural abundance). Table I lists transition frequencies from which the moments of inertia of Table II were derived by a rigid-rotor analysis.

TABLE I

MICROWAVE SPECTRUM OF DIAZIRINE[a]

Transition	Frequency, Mc. H_2CN_2	$H_2C^{15}N^{14}N$	$H_2{}^{13}CN_2$
$1_{01} \leftarrow 0_{00}$	40,394.02	39,823.36	39,192.40
$2_{11} \leftarrow 2_{12}$	20,824.34	21,028.55	19,639.87
$3_{21} \leftarrow 3_{22}$	7,944.33	8,380.85	[b]
$4_{22} \leftarrow 4_{23}$	20,992.62	21,947.91	18,648.46

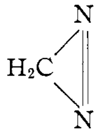
[a] The frequencies reported for $H_2C^{15}N^{15}N$ are "zeroth-order" frequencies, *i.e.*, observed frequencies corrected for quadrupole coupling effects. Transition frequencies given for the other species are averages over partially resolved fine structure components. [b] Not observed.

TABLE II

GROUND-STATE ROTATIONAL CONSTANTS (Mc) AND MOMENTS OF INERTIA (amu.-A.²) OF DIAZIRINE[a]

	H_2CN_2	$H_2C^{15}N^{14}N$	$H_2{}^{13}CN_2$
A	40,956.72	39,802.62	40,954.83
B	23,667.76	23,416.43	22,869.51
C	16,726.26	16,406.93	16,322.89
I_A	12.34305	12.70095	12.34362
I_B	21.35948	21.58873	22.10502
I_C	30.22379	30.81204	30.97068

[a] Conversion factor: $h/8\pi^2 = 505{,}531$ Mc.-amu.-A.².

Assumption of the cyclic structure  for diazirine requires that the carbon atom lie on a C_2 axis of symmetry. The fact that "A" type rotational transitions are observed for diazirine further requires that this C_2 axis be the axis of least inertia (the A-axis). An important consequence of the above is that when ^{13}C is substituted for ^{12}C, the changes ΔI in the principal moments of inertia must satisfy (in the rigid rotor approximation) the equations

$$\Delta I_A = 0 \qquad \Delta I_B = \Delta I_C \qquad (1)$$

From the assignments of Table I, we find $\Delta I_A = 0.0006$ and $\Delta I_B = 0.7456$ and $\Delta I_C = 0.7469$ amu.-Å.². A further requirement of the above assumption is that d_{NN}, the N–N bond distance, be given (again in the rigid rotor approximation) by

$$d_{NN} = [m_N{}^{-1}(I_a + I_c - I_b)]^{1/2} \qquad (2)$$

where m_N is the mass of the nitrogen atom and the I's refer to principal moments of inertia of any symmetrical isotopic species of diazirine. From our assignments for H_2CN_2 and $H_2{}^{13}CN_2$ we obtain the respective values 1.2304 Å. and 1.2305 Å. for d_{NN}. An independent determination of d_{NN} which makes

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(1) S. R. Paulsen, *Angew. Chem.*, **72**, 781 (1960).

(2) E. Schmitz and R. Ohme, *Tetrahedron Letters*, 612 (1961).

(3) W. H. Graham, *J. Am. Chem. Soc.*, **84**, 1063 (1962).

(4) The methods by which the sample was prepared and identified as diazirine are given by W. H. Graham in the previous reference.

(5) J. M. O'Reilly and L. Pierce, *J. Chem. Phys.*, **34**, 1176 (1961).