Table I. Initial First-Order Rate Constants at 20° for Spheron 6 Catalyzed Racemization of 1,1′-Binaphthyl in Acetone

Binaphthyl concn, *M*	Catalyst concn, mg/ml	I concn, $M \times 10^4$	$k_{\mathrm{obsd}} \times 10^5$, sec^{-1}
0.015	0	0	1.64
0.015	0.78	0	4.65
0.0149	1.56	0	8.41
0.0151	3.11	0	16.6
0.030	1.61	0	4.08
0.0065	1.62	0	22.7
0.0037	1.62	0	29.6
0.015	1.58	0.92[a]	5.91
0.015	1.58	1.37[a]	5.72
0.015	1.57	1.87[a]	5.44
0.015	1.57	3.78[a]	4.63
0.015	1.57	7.57[a]	3.39
0.0149	1.55	7.79[b]	1.93
0.0149	1.58	70.8[c]	7.73

[a] Naphthalene. [b] Anthracene. [c] Benzene.

reaction scheme where R and S stand for enantiomeric forms of binaphthyl, C* denotes active sites on the carbon catalyst, C*B is the catalyst–binaphthyl complex, I is an inhibitor, and C*I is the inactivated inhibitor–catalyst complex.

$$\mathrm{R} \overset{k_{\mathrm{unc}}}{\rightleftharpoons} \mathrm{S}$$

$$\mathrm{R} + \mathrm{C^*} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C^*B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{S} + \mathrm{C^*}$$

$$\mathrm{C^*} + \mathrm{I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{C^*I}$$

With the assumption of equal reactivities of R and S enantiomers (*i.e.*, $k_1 = k_{-2}$ and $k_2 = k_{-1}$) the following relationship for the observed first-order rate constants may be obtained. This type of equation for heterogeneous catalysis[12] is similar to the familiar kinetic equation for enzyme kinetics with competitive inhibition and strengthens the suggested analogy of carbon catalyzed reactions (*e.g.*, hydrogen peroxide decomposition by carbon blacks)[13] with enzymatic reactions.[3,14] Small increases in rates of racemization of binaphthyl brought about by high concentrations of complexing agents have been studied by Colter;[15] the catalysis by carbon is much more effective, with activities for a high surface carbon such as Carbolac 1 comparable with that of some enzymatic reactions.[16] The general correlation of rates with surface areas, the inhibition or poisoning by planar polyaromatic compounds, and the planar nature of the transition state for noncatalyzed racemization of binaphthyl would all seem to indicate that the active sites of these catalysts are the surface planes of the graphite-like crystallites of carbon. A flattened binaphthyl molecule on the planar surface of activated carbon is an attractive model for the transition state for catalyzed racemization. However, the possibility of reaction at more specific sites, possibly on the active edge positions of the planes, can not definitely be ruled out.

$$k_{\mathrm{obsd}} = 2k_{\mathrm{unc}} + \frac{2k_1k_2[\mathrm{C_{total}}]}{k_1[\mathrm{binaphthyl}] + 2k_2 + 2k_2k_{\mathrm{I}}[\mathrm{I}]/k_{-\mathrm{I}}}$$

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(12) J. C. Jungers and J. C. Balaceanu in "Techniques of Organic Chemistry," A. Weissberger, Ed., Vol. 8, Part 1, Interscience, New York, N. Y., 1961, pp 664–678.

(13) *E.g.*, B. R. Puri and K. C. Kalra, *Carbon* (*Oxford*), **9**, 313 (1971).

(14) V. A. Garten and D. E. Weiss, *Rev. Pure Appl. Chem.*, 7, 69 (1957).

(15) A. K. Colter and L. M. Clemens, *J. Amer. Chem. Soc.*, **87**, 847 (1965).

(16) With 0.015 *M* binaphthyl and 1.6 mg/ml of Carbolac 1 the conversion rate at 20° is 2.6×10^{-6} mol $\mathrm{min^{-1}}$ $\mathrm{mg^{-1}}$. From the average diameter of a particle of catalyst (122 Å) and with a density of 1.86 g/cm³, the average turnover number may be estimated at *ca.* 2.8×10^3 (mol of binaphthyl) $(\mathrm{min})^{-1}$ (mol of carbon particles)$^{-1}$. Enzymatic turnover numbers are in the range 1–10^6 (mol of substrate) $(\mathrm{min})^{-1}$ (mol of enzyme)$^{-1}$. The activity of a single site on carbon may be much less than that of an active site on an enzyme; however, with carbon, low individual activity is probably made up for by the presence of a great many sites on a particle.

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Photoelectron Spectra of 2,3-Diazabicyclo[2.2.*n*]alk-2-enes (*n* = 1, 2, 3, 4)

Sir:

An interesting application of photoelectron spectroscopy (pes) is the study of the interaction between nitrogen "lone pairs." Pes has been used to establish the splitting of the n_+ and n_- orbitals in *trans*-azomethane,[1] diazirine,[2] and substituted diazirines[2,3] and to examine the relative importance of through-space *vs.* through-bond interactions[4] between the "lone pairs" in 1,4-diazabicyclo[2.2.2]octane.[5] Furthermore, a recent pes study of some tetralkylhydrazines[6] indicates that the splitting of "lone pair" orbitals may, at least in some cases, reflect certain structural differences or similarities between the members of a class of related molecules.

In this communication we report a pes study of a series of cis azo molecules, namely the first four 2,3-diazabicyclo[2.2.*n*]alk-2-enes.[7]

It is evident that the pe spectra (Figure 1) of these molecules are characterized by a relatively broad band for the first IP and a somewhat sharper onset for the second band which appears to overlap with one or more

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(1) E. Haselbach, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Angew. Chem., Int. Ed. Engl.*, **8**, 878 (1969); E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **53**, 684 (1970).

(2) M. B. Robin, H. Basch, N. A. Kuebler, K. B. Wiberg, and G. B. Ellison, *J. Chem. Phys.*, **51**, 45 (1969).

(3) E. Haselbach, E. Heilbronner, A. Mannschreck, and W. Seitz, *Angew. Chem., Int. Ed. Engl.*, **9**, 902 (1970).

(4) R. Hoffmann, *Accounts Chem. Res.*, **4**, 1 (1971).

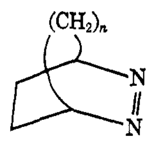
(5) P. Bischof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Tetrahedron Lett.*, 4025 (1969); E. Heilbronner and K. A. Muszkat, *J. Amer. Chem. Soc.*, **92**, 3818 (1970).

(6) S. F. Nelsen and J. M. Buschek, *J. Amer. Chem. Soc.*, **95**, 2011 (1973).

(7) The compounds **1**(*n*) were prepared and purified as described elsewhere.[8] The pe spectra were recorded on a previously described spectrometer[9] and calibrated with xenon; conventional sample handling was used for **1**(1–3) while, owing to its low volatility, **1**(4) required a direct inlet to the collision chamber and was heated to 30°.

(8) M. L. Heyman, V. T. Bandurco, and J. P. Snyder, *Chem. Commun.*, 297 (1971).

(9) J. C. Bünzli, D. C. Frost, and C. A. McDowell, *J. Electron Spectrosc. Relat. Phenomena*, **1**, 481 (1972).



1(n)

bands associated with inner IP's. By analogy with other molecules containing "lone pairs" on adjacent nitrogens, and on the basis of MO calculations,[10] we assign the first band to the ionization of the antisymmetric combination of "lone pair" orbitals n−.

Table I. Ionization Potentials (IP's, eV)[a] and Related Data for **1**(n)

	IP₁		IP₂		IP₃	Δ
n	a	v	v	$\Delta\nu^b$	v	($\epsilon_{n+} - \epsilon_{n-}$)
1	8.45	8.96	11.53	1300	11.91	2.95
2	7.79	8.32	10.70	1200	c	2.9–3.2
3	7.64	8.07[d]	10.60	1200	11.2–11.6[e]	3.1–3.5
4	7.38	8.02	(10.52)[e]		e	>2.8

[a] Key: a for adiabatic (onset of band, ±0.04), v for vertical (maximum of Franck–Condon envelope or highest vibrational peak, ±0.03). [b] Units are cm^{-1}, ±150. [c] There appear to be at least two ionizations in the 11 to 12-eV region: the first one shows two maxima at 11.20 and 11.37 eV and the second one has a maximum at 11.45 eV. [d] There is a second vibrational peak at 8.23 eV. [e] Complex bands.

Table II. N=N Stretching Frequencies $\nu_{N=N}$ (cm^{-1}),[a] Absorption Wavelengths λ_{max} (nm, eV),[b] and Extinction Coefficients ϵ for **1**(n)

	n			
	1	2	3	4
$\nu_{N=N}$	1495	1534	1562	1565
	1445	1461	1472	1474
λ_{max}	341.5, 3.63	377.5, 3.28	396.0, 3.13	383.5, 3.23
ϵ	379	188	121	119

[a] The ir spectra were recorded in CCl$_4$. [b] Measured in analytically pure hexane on a Cary-14 uv–visible spectrometer; previously reported data are λ_{max} = 341 nm (ϵ 420) for **1**(1) (S. G. Cohen, R. Zand, and C. Steel, *J. Amer. Chem. Soc.*, **83**, 2895 (1961)), and 378 nm (187) for **1**(2) (S. G. Cohen and R. Zand, *ibid.*, **84**, 586 (1962)).

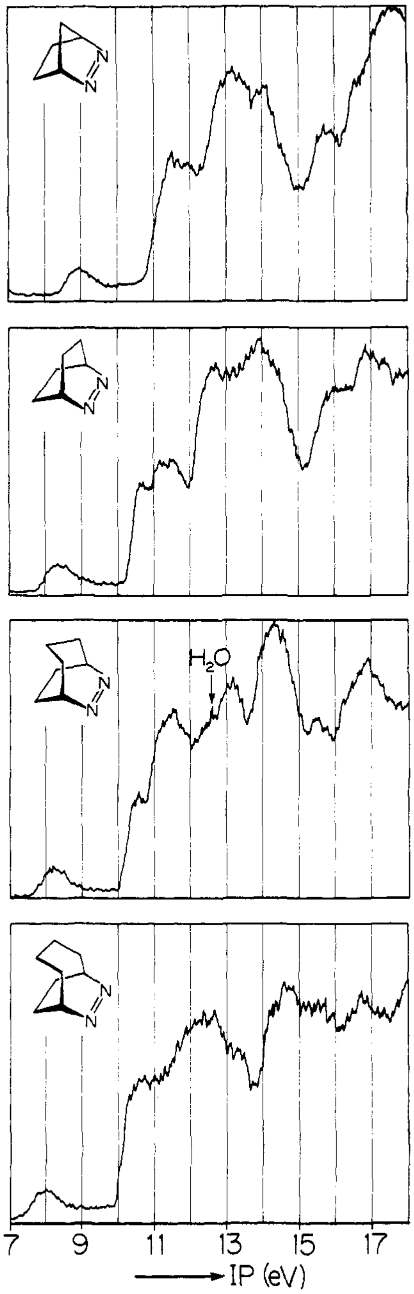


Figure 1. Pe spectra of **1**(n).

By careful analysis of the second band of each spectrum, the vibrational frequencies Δν listed in Table I can be obtained and compared with the frequencies observed for the parent molecules (Table II). The removal of a π electron from *trans*-azomethane[1] and difluorodiazirine[2] reduces the N=N stretching frequency from ~1560 cm^{-1} to 1250 and 1330 cm^{-1}, respectively. In view of these similarities, the convincing assignment for *trans*-azomethane,[1] the lack of resolvable fine structure for most of the other bands at low ionization energies, and the results of the CNDO calculations for **1**(1),[13] we assign the second band of **1**(n) to the ionization of a π electron. An unusual intensity pattern for the vibrational progression of the second band of **1**(4) is observed due to overlapping bands, and, therefore, the assignment of the peak at 10.52 eV as the vertical IP is subject to some doubt.

We assign the somewhat broad maximum in the spectrum of **1**(1) at 11.91 eV to the symmetric combination of "lone pair" orbitals. To support this assignment, we note that our calculations[14] confirm the n−, π, and n+ ordering and predict a "lone pair" orbital splitting, Δ, of 2.36 eV and a spacing of 0.97 eV between the third and fourth levels (exptl ~0.9–1.0 eV). Heilbronner[15] has independently studied the pes of **1**(1) and his assignments, which correlate well with other azo and olefinic molecules, agree with ours. The position of the n+ band is more difficult to determine for the other molecules and therefore we only list in Table I what we consider to be the likely range for Δ. We con-

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[10] Both CNDO/2 calculations[11] and CNDO calculations with an alternative set of parameters[12] were performed for **1**(1) and **1**(2) using assumed geometries.

[11] J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966).

[12] R. J. Boyd and M. A. Whitehead, *J. Chem. Soc. Dalton Trans.*, 73 (1972).

[13] The calculations for **1**(2) are less clear-cut and predict the energies of the 2nd, 3rd, and 4th levels to be within 0.12 eV.

[14] CNDO/2 also yields a good estimate of Δ for 2,3-diazabicyclo[2.2.1]heptane (calcd 1.74 eV, obsd 1.81 eV[6]).

[15] E. Heilbronner, personal communication.

clude that the splitting is quite similar throughout the series, with perhaps a slight tendency to increase as the NNC angle increases.

Indirect support for our assignment of the pes of **1**(1) can be obtained by noting that in a certain sense our assignments appear to be consistent with the pes of 2,3-diazabicyclo[2.2.1]heptane.[6] Upon forming the hydrazine derivatives of **1**(*n*), the N–N bond would be expected to lengthen and the dihedral angle between the "lone pair" orbitals would increase from 0 to about 120°. Consequently the interaction of the "lone pair" orbitals would be less. This is, in fact, confirmed by the pes of the hydrazine derivative of **1**(1) which indicates a value of 1.81 eV for Δ^6 compared with the value of 2.95 eV reported here for **1**(1).

Because of its low extinction coefficient, the observed uv transition of **1**(*n*) (*cf.* Table II) is certainly of the $n \rightarrow \pi^*$ type. Recent *ab initio* calculations[16] indicate that for cis azo compounds the $n \rightarrow \pi^*$ transition energy decreases as $\angle$NNC increases, mainly because the n_- level is destabilized while the π^* level remains approximately unchanged. Thus within a series of closely related molecules we can expect that the variation of IP_1 parallels the variation of the $n \rightarrow \pi^*$ transition energy. This is indeed the case for **1**(*n*) for which a reasonable correlation of λ_{max} (in eV) *vs.* IP_1 is observed (*cf.* Tables I and II); there is a small discrepancy for **1**(4) but slight changes in correlation energy and orbital reorganization effects prevent a strictly quantitative correlation between λ_{max} and IP_1.

Finally we would like to point out an interesting feature of the pes of all cis azo molecules that have been studied to date; the separation of the n_- and π levels is remarkably constant (about 2.5 ± 0.2 eV) whereas the splitting of the n_+ and n_- "lone pair" orbitals can be as small as 1.6 eV in 3,4-diazatricyclo[4.2.1.0^{2,5}]non-3-ene[15] or as large as 3.5 eV in diazirine.[2]

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[16] N. C. Baird, P. de Mayo, J. R. Swenson, and M. C. Usselman, *Chem. Commun.*, 314 (1973); for a discussion of the uv spectra of azo compounds see also H. Rau, *Angew. Chem., Int. Ed. Engl.*, 12, 224 (1973).

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Configuration of the β-Carbon Atoms of the β-Methyllanthionine Residues in Nisin

Sir:

β-Methyllanthionine occurs in yeast[1] and as a constituent of several interesting heterodetic polycyclic peptides, the structures of two of which have recently been elucidated.[2,3] Although the configurations of alanine and aminobutyric acid obtained after desulfurization have been determined,[2,3] the assignment at the β-carbon atom had to await comparison of the natural material with synthetic β-methyllanthionine of known configuration.

This has now been accomplished for the isomer occurring in nisin,[2] and several observations have been made pertaining to the problem in general.

Starting materials for the synthesis of the isomers of β-methyllanthionine are the diastereoisomeric pairs A and B of DL-β-methyl-*S*-benzylcysteine prepared by the addition of benzylmercaptan to the azlactone of benzoyldehydrobutyrine followed by fractional crystallization and hydrolysis of the products.[4] The configurational identities were determined by application of the cyanogen bromide reaction[5] to the *N*-acetyl-β-methyl-*S*-methylcysteines. The benzyl group was removed by reaction with anhydrous hydrogen fluoride (HF) for 1 hr at room temperature in the presence of anisole. After evaporation of the HF and washing with ethyl acetate, the amino acids were *S*-methylated by treatment with methyl-*p*-nitrobenzene sulfonate in 0.05 *M* phosphate buffer (pH 8.5) under nitrogen. The *S*-methyl derivatives were treated with a fourfold excess of acetic anhydride at the same pH, and sufficient 88% formic acid was added to give a 60% formic acid solution. Exposure to 3 equiv of cyanogen bromide at room temperature for 2 days resulted in the transformation of 50% of the acetyl-DL-β-methyl-*S*-methylcysteine A to 97% pure DL-*O*-acetyl-*allo*-threonine (Figure 1) while the amino acids B, correspondingly yielded DL-*O*-acetylthreonine of identical configurational purity.

The identity of the products was determined by comparison of their elution volumes from cation exchange resin columns (0.9 × 60 cm, 53°, 0.2 *N* sodium citrate buffer, pH 3.25) with those of authentic samples prepared from DL-threonine and DL-*allo*-threonine by treatment with 1 *N* HCl in glacial acetic acid and crystallization from alcohol–ether. Since an inversion of configuration at the β-carbon atom is expected in the cyanogen bromide reaction (Figure 1), the pair designated A must be the DL-threo amino acids, while B are the DL-allo isomers.

The β-methyllanthionines were obtained from the reaction of the β-methylcysteines with *N*-formyl-L-β-chloroalanine.[6] The latter was prepared by dissolving L-chloroalanine hydrochloride in anhydrous formic acid, adding 1 equiv of sodium bicarbonate and 20 equiv of preformed formic acetic anhydride[7] at 10° in two portions separated by a 2-hr interval. The mixture was lyophilized after 4 hr and the product allowed to react with the thiol amino acids in 0.05 *M* phosphate buffer (pH 8.5) under nitrogen. The formyl group was removed with 6 *N* HCl in 10 min at 100°.[8] Amino

[1] P. Downey and S. Black, *J. Biol. Chem.*, **228**, 171 (1957).

[2] E. Gross and J. L. Morell, *J. Amer. Chem. Soc.*, **93**, 4634 (1971).

[3] E. Gross, H. H. Kiltz, and E. Nebelin, *Hoppe-Seyler's Z. Physiol. Chem.*, **354**, 810 (1973).

[4] H. E. Carter, C. M. Stevens, and L. F. Ney, *J. Biol. Chem.*, **139**, 247 (1941).

[5] E. Gross, *Methods Enzymol.*, **11**, 238 (1966).

[6] β-Chloroalanine not protected at the amino group reacts *via* aziridine intermediates to generate undesired products resulting from the addition of sulfhydryl groups to the α-carbon atom.

[7] V. C. Mehlenbacher, *Org. Anal.*, **1**, 37 (1953).