

molecule. Experiments employing UV/visible laser-induced fluorescence to probe the vibrational populations of molecules pumped by powerful CO₂ TEA lasers (megawatt power levels) have recently been reported.³⁶⁻⁴⁰ The preliminary results suggest, as expected, that energy transfer in highly excited molecules is quite fast; nevertheless, the detailed competition between various energy-transfer pathways has not yet been mapped out. Future experiments are expected to unravel more completely many of the features of vibrational-energy transfer in complex, highly excited molecules. In principle this same technique, which has inherently much higher resolution than infrared laser fluorescence methods, can also be used to measure energy-transfer rates from a specific vibration-rotation level $|vJ\rangle$ of one mode to a specific vibration-rotation level $|v'J'\rangle$ of a second mode.

Concluding Remarks

Sufficient vibrational energy transfer data have now been obtained to provide a relatively simple picture of intermode vibrational energy flow processes in small,

(36) D. M. Brenner and K. Brezinsky, *Chem. Phys. Lett.*, **67**, 36 (1979).

(37) D. M. Brenner, K. Brezinsky, and P. M. Curtis, *Chem. Phys. Lett.*, **72**, 202 (1980).

(38) D. M. Brenner, *J. Chem. Phys.*, to be published.

(39) D. M. Brenner, *J. Chem. Phys.*, to be published.

(40) D. M. Brenner, *J. Chem. Phys.*, to be published.

weakly excited molecules. Energy transfer within a given mode is very rapid due to collisional ladder climbing processes which bring the mode into a nonequilibrium steady state. Spillover of energy from one mode to another is usually dominated by a single energy-transfer channel between distinct low-lying vibrational states of the different modes. Channels which minimize the amount of vibrational energy released to or taken from the translational/rotational energy bath and which minimize the number of vibrational quanta exchanged in the energy-transfer process tend to be favored. Anharmonic mixing of levels increases significantly the probability of energy transfer between states which formally require the exchange of more than two vibrational quanta to proceed. Much experimental work remains to be done before the complex energy-transfer pathways of strongly excited small molecules or even weakly excited large molecules in their ground electronic state can be unravelled.

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A Systematic Look at Weakly Bound Diatomics

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A little more than 100 years ago, Johannes van der Waals proposed his celebrated equation of state for a real gas.¹ This equation incorporated two parameters to represent the macroscopic effects of intermolecular repulsions (molecular size) and intermolecular attractions. Comparisons among these parameters constituted one of the first systematic attempts to organize, interpret, and understand variations in weak intermolecular bonding from molecule to molecule.

What should one expect to learn from weak bonding? By ordinary chemical standards, such bonds are ridiculously weak. As a consequence, most of chemical thought is organized around an understanding of strong chemical forces. Terms such as covalent bond, donor-acceptor bond, hydrogen bond, charge delocalization, and the like conjure specific models with a host of

well-understood consequences. Weakly bound molecules have historically not been thought of in these terms, but it is not at all obvious where one draws (or even if one should draw) the line separating molecules into categories based on bond energies.

Nevertheless, weakly bound molecules have a well-defined set of bound quantum levels which can be analyzed by methods familiar to the realm of stable chemical compounds. Can such analyses expose the origins of weak bonding in greater detail? Can weak bonding be described *without* recourse to the terminology of chemical bonding, or are there clear examples of molecules for which this language is *essential*, despite the weakness of the interaction? In this account we discuss recent attempts to answer these and related questions.

Families of Weakly Bound Diatomics

A cursory glance through the periodic table leads one to predict most of the weakly bound homonuclear dia-

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(1) J. D. van der Waals, "Over de continuïteit van den gas- en vloeistofoestand," Thesis, Leiden, 1873. An interesting account of van der Waals' early work is given by M. J. Klein, *Physica*, **73**, 28 (1974).

Table I
Binding Energies of Weakly Bound Diatomics (in cm^{-1})^a

molecule	D_e^b	atomic ground-state configuration	ref
He ₂	7.65 ± 0.15	1s ²	c
Ne ₂	29.7 ± 2	ns ² np ⁶	9
Ar ₂	100 ± 1	ns ² np ⁶	2
Kr ₂	140 ± 2	ns ² np ⁶	d
Xe ₂	196 ± 2	ns ² np ⁶	d
Rn ₂	(250)	ns ² np ⁶	d
Be ₂	800 ± 80	ns ²	3
Mg ₂	430 ± 1	ns ²	3
Ca ₂	1095 ± 0.5	ns ²	3
Sr ₂	1100 ± 100	ns ²	3
Ba ₂	(2000)	ns ²	8
Ra ₂	(1400)	ns ²	8
Zn ₂	1400 ± 300	(n - 1)d ¹⁰ ns ²	3
Cd ₂	760 ± 150	(n - 1)d ¹⁰ ns ²	3
Hg ₂	630 ± 100	(n - 1)d ¹⁰ ns ²	3
Mn ₂	3500 ± 2000	3d ⁵ 4s ²	5
Eu ₂	2800 ± 1400	4f ⁷ 6s ²	7
Yb ₂	1400 ± 1400	4f ¹⁴ 6s ²	7
Pu ₂ , Am ₂	(2000)	5f ^x 6d ⁰ 7s ²	8
Bk ₂ -No ₂	(1500)	5f ^x 6d ⁰ 7s ²	8

^a Values in parentheses are estimated. ^b See ref 4 and 6. Values in cm^{-1} . ^c J. M. Farrar and Y. T. Lee, *J. Chem. Phys.*, **56**, 5801 (1972). ^d J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, *ibid.*, **61**, 3081 (1974); K. K. Docken and T. P. Schafer, *J. Mol. Spectrosc.*, **46**, 454 (1973).

tomics. Certainly, the rare gas dimers He₂ through Rn₂ are the best known examples. In fact, the interatomic potential function for Ar₂ is as well characterized² as that for many common stable diatomics. The next-best known family³ is the group 2 metal dimers: the alkaline earth diatomics, and Zn₂, Cd₂, and Hg₂. The ground-state atoms have closed (s²) configurations, and a formal analogy to rare gas dimers is predicted. However, as one proceeds atom by atom from the dimer to the bulk, these species revert to strongly bound metals due to the presence of low-lying sp or ds configurations. The possible role such configurations may have in the dimer bond will be discussed below.

Less obvious weakly bound homonuclear diatomics can be found scattered about the periodic table. Atomic Mn has a 3d⁵4s² configuration in its ground state. The stability of the d⁵ configuration in this first row transition element leads to an anomalously weak binding energy^{4,5} for Mn₂: $D_e \sim 0.4 \pm 0.25$ eV (or $\sim 3500 \pm 2000$ cm^{-1}). Similarly, the stability of the 4f⁷6s² configuration of Eu and the 4f¹⁴6s² configuration of Yb yields anomalously weak binding,⁷ and the actinide

(2) J. M. Parson, P. E. Siska, and Y. T. Lee, *J. Chem. Phys.*, **56**, 1511 (1972); E. A. Colbourn and A. E. Douglas, *ibid.*, **65**, 1741 (1976); J. A. Barker, R. A. Fisher, and R. O. Watts, *Mol. Phys.*, **21**, 657 (1971); J. H. Goble, S. M. Walsh, and J. S. Winn, unpublished results.

(3) See, in general, (a) J. H. Goble and J. S. Winn, *Chem. Phys. Lett.*, **77**, 168 (1981); (b) Be₂: B. Liu and A. D. McLean, *J. Chem. Phys.*, **72**, 3418 (1980); (c) Mg₂: C. R. Vidal and H. Scheingraber, *J. Mol. Spectrosc.*, **65**, 46 (1977); (d) Ca₂: C. R. Vidal, *J. Chem. Phys.*, **72**, 1864 (1980); (e) Sr₂: T. Bergeman and P. F. Liao, *ibid.*, **72**, 886 (1980); (f) Zn₂: K. D. Carlson and K. R. Kushnir, *J. Phys. Chem.*, **68**, 1566 (1964); (g) Cd₂ and Hg₂: see both the previous reference and ref 8 and 17.

(4) All bond energies used in this Account are true well depths, D_e , rather than 0-K dissociation energies, D_0 , in order to remove the zero point energy.

(5) K. A. Gingerich, *J. Cryst. Growth*, **9**, 31 (1971).

(6) All energies are reported in cm^{-1} units. Conversions were made by using $hc/k = 1.4388$ cm^{-1} K, $R = 8.3143$ $\text{J K}^{-1} \text{mol}^{-1}$, 4.184 J cal^{-1} , and 8065.5 $\text{cm}^{-1} \text{eV}^{-1}$.

dimers Pu₂, Am₂, and Bk₂ through No₂ are expected to be weakly bound due to the bonding ineffectiveness of the highly localized 5f electrons.⁸

Table I summarizes these diatomics. One can see that weak bonding can result from a variety of atomic configurations, not necessarily limited to closed principal shell configurations. Moreover, binding energies are found throughout a two order of magnitude range. In general, these energies increase as one moves down a periodic group, in contrast to the behavior of chemically bound diatomics, for which the energies generally decrease.

A sufficiently large number of heteronuclear dimers have been studied to allow one to note certain trends. The majority of these dimers contain at least one rare gas, and the heteronuclear rare gas dimers are the prototypes. They provided the first arena in which simple combination rules could be tested (and found to be inaccurate).⁹ Three other classes that are well studied are the rare gas monohalides, the rare gas alkali metal dimers, and certain molecular ions. The bonding in the monohalides, especially XeF, is of importance to one's basic understanding of the requirements for chemical bonding. Four of these (XeF, XeCl, KrF, and ArF) are the active species in UV excimer lasers, the emission from which is to the weakly bound ground state. The rare gas alkalis are also open-shell dimers, dominated by the single alkali valence electron. NaAr¹⁰ and NaNe¹¹ are the best characterized examples. These molecules have exceptionally weak bonds and long bond lengths. For instance, $D_e = 41$ cm^{-1} and $R_e = 4.99$ Å for NaAr. These values are striking, especially when compared to Ar₂ ($D_e = 100$ cm^{-1} , $R_e = 3.76$ Å) or NeAr ($D_e = 50$ cm^{-1} , $R_e = 3.43$ Å).

The rare gas alkaline earth cations BeAr⁺, BeKr⁺, BeXe⁺, and CaAr⁺ are known from emission spectra.¹²⁻¹⁵ These ions form an interesting contrast to the isovalent rare gas alkalis, since these families differ by the presence or absence of a localized charge on the metal atom. The mixed rare gas ion HeNe⁺ is also known from emission spectra.¹⁶ There are very few data on other mixed rare gas dimer cations,¹⁷ but those between atoms of greatly different ionization potential are expected to be weakly bound. Certain rare gas alkali ions have been studied in scattering experiments

(7) A. Kant and S. S. Lin, *Monatsh.*, **103**, 751 (1972).

(8) L. Brewer and J. S. Winn, *Proc. Faraday Symp.*, No. 14, 126 (1980).

(9) C. Y. Ng, Y. T. Lee, and J. A. Barker, *J. Chem. Phys.*, **61**, 1996 (1974).

(10) J. Tellinghuisen, A. Rangone, M. S. Kim, D. A. Auerbach, R. E. Smalley, L. Wharton, and D. H. Levy, *J. Chem. Phys.*, **71**, 1283 (1979); J. H. Goble and J. S. Winn, *ibid.*, **70**, 2051 (1979); R. E. Smalley, D. A. Auerbach, P. S. H. Fitch, D. H. Levy, and L. Wharton, *ibid.*, **66**, 3778 (1977).

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(12) (a) J. H. Goble, D. C. Hartman, and J. S. Winn, *J. Chem. Phys.*, **67**, 4206 (1977); (b) K. V. Subbaram, J. A. Coxon, and W. E. Jones, *Can. J. Phys.*, **54**, 1535 (1976); (c) R. J. LeRoy and W.-H. Lam, *Chem. Phys. Lett.*, **71**, 544 (1980).

(13) J. A. Coxon, W. E. Jones, and K. V. Subbaram, *Can. J. Phys.*, **55**, 254 (1977).

(14) J. A. Coxon, W. E. Jones, and K. V. Subbaram, *Can. J. Phys.*, **53**, 2321 (1975).

(15) D. C. Hartman and J. S. Winn, *J. Chem. Phys.*, **74**, 4320 (1981).

(16) I. Dabrowski and G. Herzberg, *J. Mol. Spectrosc.*, **73**, 183 (1978).

(17) K. P. Huber and G. Herzberg, "Constants of Diatomic Molecules", Van Nostrand-Reinhold, New York, 1979.

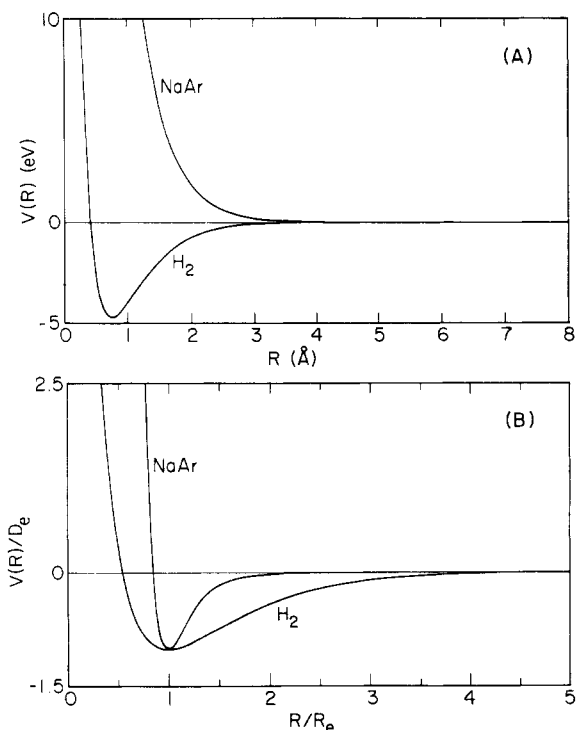


Figure 1. (a) Potential-energy curves for the ground electronic states of H_2 and $NaAr$. The potential well for $NaAr$ has its minimum at 5 Å, but being only 5 meV deep, it is invisible on this drawing. (b) Potential curves redrawn in reduced coordinates. Note the relative narrowness of the $NaAr$ potential compared to the H_2 potential.

at low enough energy to be sensitive to the well region of the potential.¹⁸⁻²⁰

Potential Energy Functions for Weakly Bound Diatomics

For an understanding of the weakly bound diatomics in greater detail than that afforded by dissociation energies and bond lengths, an analysis of the full interatomic potential function²¹ is necessary. In Figure 1a, the potential functions for the ground states of the strongly bound diatomic H_2 and the weakly bound diatomic $NaAr$ are drawn on the same scale. This example is admittedly exaggerated, and since the ratio of dissociation energies is nearly 1000:1, the minimum in the $NaAr$ potential cannot be seen. In fact, the ratio of bond lengths is 0.74:5, and the $NaAr$ potential well is capable of supporting six vibrational levels.¹⁴

To emphasize the well region and to facilitate comparisons of the *relative* differences among many potential functions, it is instructive to plot these functions in a reduced coordinate system, scaling lengths by the equilibrium bond length, R_e , and energies by the dissociation energy, D_e . When Figure 1a is replotted in these coordinates, Figure 1b results. One is struck im-

(18) See, for example, F. E. Budenholzer, E. A. Gislason, and A. D. Jorgensen, *J. Chem. Phys.*, **66**, 4832 (1977).

(19) E. Böttner, W. L. Dimpfl, U. Ross, and J. P. Toennies, *Chem. Phys. Lett.*, **32**, 197 (1975).

(20) A. Ding in "Interactions Between Ions and Molecules", P. Ausloos, Ed., Plenum, New York, 1975; A. Ding, J. Karlau, J. Weise, J. Kendrick, P. J. Kuntz, I. H. Hillier, and M. F. Guest, *J. Chem. Phys.*, **68**, 2206 (1978).

(21) The phrase "full interatomic potential function" stands for the Born-Oppenheimer total energy as a function of internuclear separation. Nonadiabatic effects are generally unknown among weakly bound species, except in certain types of excited states. See ref 11 and 16 for examples.

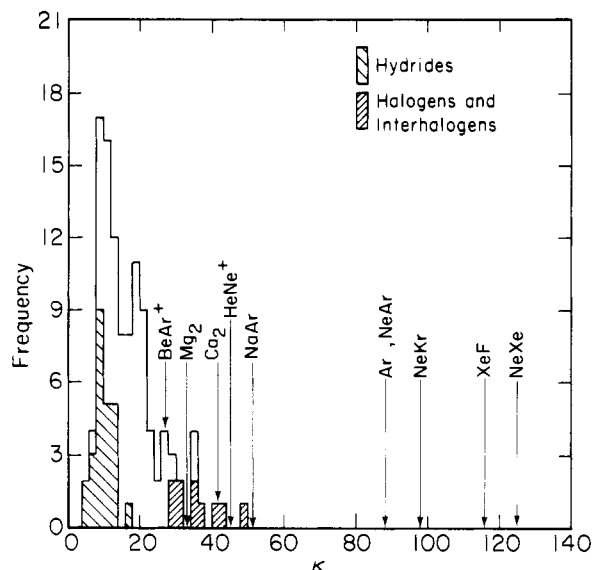


Figure 2. A histogram of reduced curvature values.

mediately by the relative narrowness of the $NaAr$ potential.

This behavior is a rather general trait of weakly bound molecules. The fundamental parameter of such plots is the reduced curvature of the potential at R_e . This quantity, denoted κ , is defined by

$$\kappa = \frac{R_e^2}{D_e} \left(\frac{d^2V(R)}{dR^2} \right)_{R_e} = \frac{R_e^2}{D_e} k_e \quad (1)$$

In terms of spectroscopic constants,

$$\kappa = \frac{\omega_e^2}{2B_e D_e} \quad (2)$$

where ω_e is the equilibrium harmonic vibration constant and B_e is the equilibrium rotation constant. If one consults a standard compilation of diatomic spectroscopic constants¹⁷ and computes κ values where sufficiently accurate data are available, a histogram, shown in Figure 2, can be made and compared to κ values for weakly bound diatomics. Note first that, for chemically bound species, κ is confined to a tight range of values. Hydrides cluster at the low end of this range, and halogens cluster at the high end. The near constancy of κ , or, to a better approximation, the periodic variations of κ , are at the heart of a number of empirical rules²² relating force constants, bond lengths, and dissociation energies in various ways. Representative κ values for weakly bound molecules are generally large to enormous in comparison.

The next region of the potential worth scrutiny is the attractive tail. The behavior of the potential at very large R has been well understood for some time²³ in terms of a long-range expansion of electrostatic, induction, and dispersion forces. This is at once a blessing and a bane. Surely at very large interatomic distances these theories are correct, but at what distance do they begin to fail significantly? How long is "long range"? How can *equilibrium* measurements be related to a

(22) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1933); **3**, 710 (1934); D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **35**, 458 (1961); H. S. Johnston, *J. Am. Chem. Soc.*, **86**, 1644 (1964).

(23) J. O. Hirschfelder, C. F. Curtiss, and B. R. Bird, "Molecular Theory of Gases and Liquids", Wiley, New York, 1954.

portion of the potential which is physically removed from the equilibrium region?

To answer these questions, one must have a method for obtaining interatomic potential functions from spectroscopic, scattering, or bulk property data, and, ideally, the method should *not* be constrained to a priori expectations about the shape of the attractive tail of the potential. (One can, of course, use ab initio methods to calculate the potential directly, and several such calculations have appeared.²⁴) The first step in any inversion method is to decide, in one way or another, on a functional form for the potential. Virtually every analytic function which has a steep repulsive wall, a single minimum, and a smooth rise to dissociation has been suggested as a model function. Many of these can be rejected on the basis of their inability to approximate even crudely the correct long range attraction. The simplest that remain are the Lennard-Jones (m, n) potentials,

$$V(R) = \mathcal{D}_e \left\{ 1 + \frac{nm}{n-m} \left[\frac{1}{n} \left(\frac{R_e}{R} \right)^n - \frac{1}{m} \left(\frac{R_e}{R} \right)^m \right] \right\} \quad (3)$$

the Morse potentials,

$$V(R) = \mathcal{D}_e \{ 1 - \exp[-\beta(R - R_e)] \}^2 \quad (4)$$

and the ($\exp-n$) potentials

$$V(R) = \mathcal{D}_e \{ 1 + A \exp(-BR) - C_n/R^n \} \quad (5)$$

Numerous variations exist, as do many types of piecewise analytic forms,² where several different functions are splined together to give a continuous, multiparameter function defined for all R . Multiparameter splined functions lack a certain uniqueness. One must make often arbitrary decisions as to where one function ends and the next begins. This is especially disadvantageous if one is concerned with the question, how long is "long range"?

If the data consist of spectroscopic term values, the well-established RKR method²⁵ may be used to compute the inner and outer classical turning points of the rotationless level of each observed vibrational level. Extrapolation of these data to unobserved vibrational levels generally requires some assumption about the potential function's R dependence. The result is a tabulated potential function which is difficult to interpret by itself or to compare to other molecules. The RKR points can be fit to any suitable analytic function, of course, but it would seem advantageous to begin an analysis with such a function if one wishes to establish comparisons.

We have therefore chosen to use an analytic potential function which has the capabilities of avoiding piecewise analyticity while answering many questions concerning the shape of the potential well not only near R_e but also at large R . Thus function, first suggested by Thakkar²⁶ in 1975, is a straightforward extension of the familiar expansion introduced by Dunham²⁷ in 1932. Dunham considered an expansion about the point $R = R_e$ in terms of the variable $(R - R_e)/R_e$. This expansion

cannot converge for $R > 2R_e$, and it is therefore of little use for our purposes.

The Thakkar function avoids this problem. It is written

$$V(R) = e_0 \lambda^2 \left[1 + \sum_{n=1}^{\infty} e_n \lambda^n \right] \quad (6)$$

where

$$\lambda = \text{sgn}(p) [1 - (R_e/R)^p] \quad (7)$$

and $\text{sgn}(p) = +1$, $p > 0$, or -1 , $p < 0$. If $p \equiv -1$, the Dunham potential results. If $e_n = 0$, $n = 1, 2, 3, \dots$, the Lennard-Jones ($p, 2p$) potential results (with $e_0 = \mathcal{D}_e$; compare eq 3 with $n = 2m$). In general, p is simply a nonzero parameter which we are free to vary, along with the e_n 's. Thakkar argued that one could choose p by a criterion which is optimum in several ways. This criterion may be written²⁸ in terms of the second and third derivatives of $V(R)$ at R_e by choosing p such that

$$p = -\frac{\ell_e R_e}{3k_e} - 1 \quad (8)$$

(where ℓ_e is the third derivative). In terms of the first Dunham potential coefficient, a_1 , p may be written

$$p = -a_1 - 1 \quad (9)$$

or in terms of equilibrium spectroscopic constants

$$p = \alpha_e \omega_e / 6B_e^2 \quad (10)$$

In eq 10, α_e is the vibration-rotation interaction constant, relating²⁹ the rotational constant for level v to the equilibrium rotational constant via

$$B_v = B_e - \alpha_e(v + 1/2) \quad (11)$$

This choice of p causes the leading term of eq 6 to reproduce both k_e and ℓ_e exactly. It also forces the first correction parameter, e_1 , to be zero, and it is the correct expression for p when the true potential is just a simple Lennard-Jones type. Thus, the Thakkar potential with this choice for p is essentially an expansion in a series of Lennard-Jones functions.

Note that p has considerable physical significance. The potential function approaches dissociation as a polynomial lead by R^{-p} . This behavior holds the promise that eq 6 can approximate the anticipated long-range behavior of a weakly bound species. However, as eq 8 shows, p is directly calculated from the *equilibrium* properties of the potential function.

We have obtained the Thakkar potential constants for a variety of weakly bound molecules.^{2,3,10,12,24} Throughout the well region, the Thakkar function is superior to the Dunham function or the Simons-Parr-Finlan function³⁰ (which is just a Thakkar potential with $p \equiv +1$) and is roughly as good as the Huffaker-Morse potential³¹ (except at long range, where a Morse functionality is usually poor) or an RKR potential.²⁵

One fault of the Thakkar function is occasional nonphysical behavior at the repulsive wall. Certain sets

(28) J. H. Goble and J. S. Winn, *J. Chem. Phys.*, **70**, 2058 (1979).

(29) Strictly speaking, one should use Dunham Y_{ij} terms instead of simple mechanical constants, as discussed in ref 26. The differences between the two sets of constants is small, and I have used the more familiar mechanical constant symbols here for convenience.

(30) G. Simons, R. G. Parr, and J. M. Finlan, *J. Chem. Phys.*, **59**, 3229 (1973).

(31) J. N. Huffaker, *J. Chem. Phys.*, **64**, 3175 (1976); **64**, 4564 (1976).

(24) See, for example, R. P. Saxon, R. E. Olson, and B. Liu, *J. Chem. Phys.*, **67**, 2692 (1977), and ref 3b.

(25) R. Rydberg, *Z. Phys.*, **73**, 376 (1931); **80**, 514 (1933); O. Klein, *ibid.*, **76**, 226 (1932); A. L. G. Rees, *Proc. R. Soc. London*, **59**, 998 (1947).

(26) A. J. Thakkar, *J. Chem. Phys.*, **62**, 1693 (1975).

(27) J. L. Dunham, *Phys. Rev.*, **41**, 721 (1932).

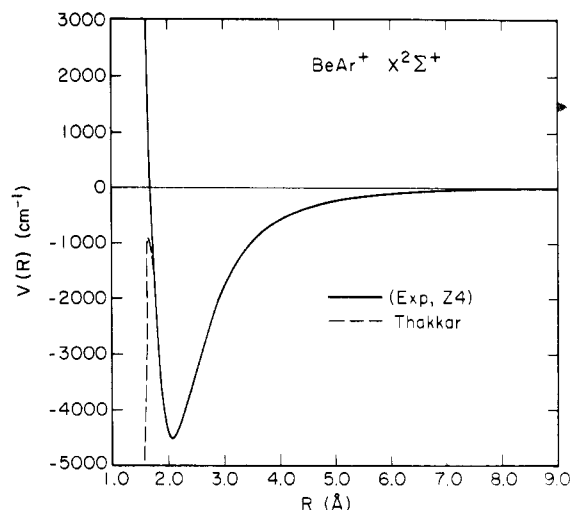


Figure 3. Potential curves for $\text{BeAr}^+ X^2\Sigma^+$. The solid line is an (EXP-Z4) potential fit to a six-parameter Thakkar function (dashed line) obtained by spectroscopic inversion. From the point where the two curves meet (near 1.0 Å) to larger R , the two functions are virtually identical.

of parameters which otherwise reproduce the equilibrium and long-range regions of the potential sometimes cause the repulsive wall to appear (or disappear, to be more accurate), as shown by the dashed curve in Figure 3. Here, the Thakkar function for $\text{BeAr}^+ X^2\Sigma^+$ is compared to a model potential^{12,15} devised for this family of molecules, the (exp-Z4) potential

$$V(R) = A \exp(-BR) - Z^2 e^2 \alpha / 2R^4 \quad (12)$$

where α is the polarizability of Ar, e is the elementary charge, and A , B , and Z are variable parameters. Z is interpreted as the *effective* nuclear charge on Be^+ to account for partial overlap and deshielding by the 2s electron of Be^+ . For this molecular state, $Z = 1.29$, and the model potential is virtually identical with the Thakkar function, except at the repulsive wall.

The potential function for BeAr^+ was derived from data on the lowest five vibrational levels of the molecule. Classical motion in these levels is confined to the range $R = R_e + 0.50 \text{ Å}$ to $R_e - 0.25 \text{ Å}$ (with $R_e = 2.0855 \text{ Å}$), i.e., highly localized near R_e . Nevertheless, the long-range induction forces (and their distance dependence) are recoverable from such localized data, at least for this molecule, and one is confident in stating that BeAr^+ is bound by little more than the polarizing effects of Be^+ and, more importantly, that these effects continue to dominate near R_e .

For $\text{BeAr}^+ X^2\Sigma^+$, one finds $p = 3.156$. How can one recognize that this is, in some sense, a special or an anticipated value? First, 3.156 is close to but less than the asymptotic induction exponent of 4. The polynomial nature of eq 6 requires p to be different from the anticipated integral leading exponent (call it n), and we have found p to be in the range n to $n - 1$ when long-range forces persist near R_e .

A more interesting test comes when one computes p values (via eq 10) for chemically bound diatomics and compares these to p values for weakly bound diatomics, as is shown in Figure 4. Note that chemically bound diatomics have p values in the range 1–3, clustered sharply near $p = 2$, while p values for weakly bound systems extend throughout the range 3–7. On comparing Figures 2 and 4, one notes that p and κ are

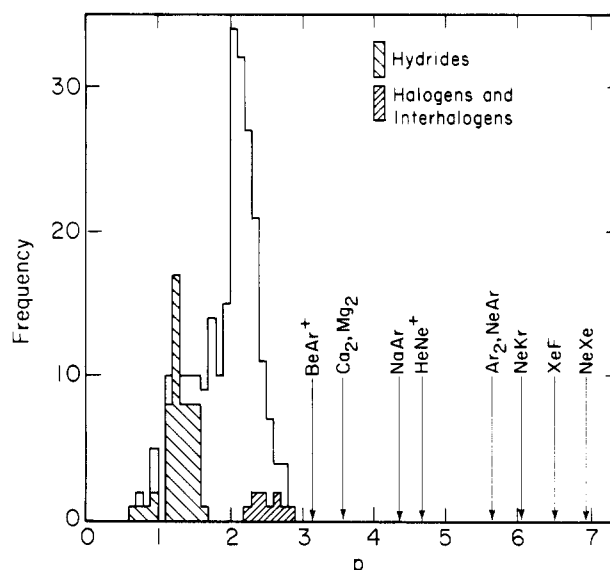


Figure 4. A histogram of p values.

somewhat correlated, even for chemically bound species. One can use eq 1 and 8 to derive an expression for the reduced third derivative of the potential, yielding

$$\lambda_e \equiv \frac{R_e^3}{\mathcal{D}_e} \ell_e = -3\kappa(p + 1) \quad (13)$$

From Figures 2 and 4 and this expression, one can see that the weak bond is relatively more anharmonic than the chemical bond. (A somewhat related phenomenon is the fact that the zero point energy of a weakly bound molecule is typically a much greater fraction of the bond energy than for a chemically bound molecule. For instance, for Ar_2 , the level $v = 0$ is found 15% of the way up the potential well. The corresponding figures for Cl_2 , K_2 , and the light H_2 molecule are 1.4%, 1.1%, and 5.7%, respectively.)

A Physical Interpretation of Potential Parameters

One can generate these functions and tabulate their parameters, but at some point, one is obliged to remember exactly what these functions are supposed to be representing and to interpret the parameters accordingly. The phrase “potential energy function” usually, and certainly in the context of this article, means the Born–Oppenheimer total energy of both atoms as a function of R . Two opposing effects combine to produce binding: the variation with R of the total Coulombic potential energy and the variation with R of the total kinetic energy of the electrons. One can discuss any type of diatomic bond in these terms by means of the virial theorem.³²

Let $\langle \text{PE} \rangle$ be the expectation value of the total Coulombic potential energy operator (which is a function of R) and let $\langle \text{KE} \rangle$ be the expectation value of the operator for the total kinetic energy of the electrons (also a function of R). The virial theorem states

$$\langle \text{PE} \rangle = 2V(R) + R \frac{dV(R)}{dR} \quad (14)$$

and

(32) J. C. Slater, *J. Chem. Phys.*, 1, 687 (1933).

$$\langle \text{KE} \rangle = -V(R) - R \frac{dV(R)}{dR} \quad (15)$$

Therefore, given any accurate $V(R)$, one can deduce the functions $\langle \text{PE} \rangle$ and $\langle \text{KE} \rangle$. These functions are more illuminating than $V(R)$ alone when one wishes to discuss the changes in electronic structure that occur on binding.

Qualitatively, $\langle \text{PE} \rangle$ and $\langle \text{KE} \rangle$ behave as follows for any bound diatomic, with the exception of purely ionic attraction. As the atoms approach, $\langle \text{PE} \rangle$ begins to rise, but $\langle \text{KE} \rangle$ falls at a greater rate. At some distance, $\langle \text{KE} \rangle$ reaches a minimum and begins to rise. At a slightly smaller distance, $\langle \text{PE} \rangle$ reaches a maximum and begins to fall. These trends continue up to $R = R_e$ where the decrease in $\langle \text{PE} \rangle$ is exactly twice the increase in $\langle \text{KE} \rangle$. For $R < R_e$, $\langle \text{KE} \rangle$ continues to increase and $\langle \text{PE} \rangle$ to decrease until at some $R \ll R_e$, $\langle \text{PE} \rangle$ finally begins to increase due to nuclear-nuclear repulsion.

A distinguishing feature of weakly bound diatomics, when viewed in terms of the virial theorem, is the persistence of the initial behavior ($\langle \text{PE} \rangle$ rising, $\langle \text{KE} \rangle$ falling) to R values quite near R_e followed by a very rapid switch of these trends. It is easy to show³³ that

$$\left(\frac{d\langle \text{PE} \rangle}{dR} \right)_{R_e} = - \left(\frac{d\langle \text{KE} \rangle}{dR} \right)_{R_e} = k_e R_e \quad (16)$$

$$\left(\frac{d^2\langle \text{PE} \rangle}{dR^2} \right)_{R_e} = (1 - 3p)k_e \quad (17)$$

and

$$\left(\frac{d^2\langle \text{KE} \rangle}{dR^2} \right)_{R_e} = 3pk_e \quad (18)$$

where eq 8 is the relevant definition for p . One can see from these relations and from the data in Figures 2 and 4 that, near R_e , $\langle \text{KE} \rangle$ is increasing and $\langle \text{PE} \rangle$ decreasing at *relatively* much greater rates for weakly bound species (κ and p both large) than for chemically bound species.

All of these observations indicate that weakly bound molecules establish their equilibrium position over a relatively shorter distance (when distance is measured in units of R_e) than do chemically bound molecules and that the onset of repulsion is relatively more abrupt for a weak bond. These effects are what one expects in the absence of extensive charge delocalization during bonding. But even among weakly bound diatomics themselves, curious variations are found in the degree to which long-range forces persist toward R_e , in the relative rates at which repulsive forces appear, and in the failure of homologous families to display simple trends in bond energies or bond lengths.

Table II presents the evidence. In this table, bond energies, lengths, κ , and p values have been collected from various sources as indicated. Note that different model potentials can exhibit rather different shape parameters (κ and p) while still reproducing the type of data to which the model was fit. Few potentials have been compared to a truly wide variety of data types (such as bulk properties, differential scattering, spectroscopic, etc.), and fewer still have been constructed from direct spectroscopic observation of many bound

levels, making some of the data in Table II uncertain if only because of model dependency.

Now we look at a few specific examples. First, compare Ar_2 with NaAr . The strong bond in Na_2 and the greater polarizability of Na might lead one to expect NaAr to be more strongly bound than Ar_2 and to have a shorter bond length. How can one understand why neither expectation is realized? At long range, the NaAr potential function must fall at a greater rate than the Ar_2 potential because of the greater dispersion interaction. But the virial theorem indicates that repulsion involves an abrupt increase in electron kinetic energy near R_e . The 3s electron on Na is spatially quite diffuse, and when it first encounters the Ar atom (i.e., when electron overlap becomes appreciable), this electron will increase its kinetic energy. The effect is analogous to confining a particle in a box and then slightly decreasing the box dimensions. Since the 3s electron is diffuse, the encounter occurs at a large distance, before the attractive dispersion force has had an opportunity to become appreciable. Near R_e , Ar is moving under the influence of this single diffuse electron. Hence, the long-range shape of the potential is lost (p is much smaller than 6) and the curvature of the potential is relatively gentle (κ is 51). Note that the bond length for NaNe is *larger* than that for NaAr . This is to be expected, since the NaNe attraction is weaker than for NaAr , but the 3s repulsion should grow at roughly the same rate for both molecules.

Next, we turn to the alkaline earth diatomics and the alkali-mercury diatomics.³⁴ It is here we encounter "first row anomalies" in the species Be_2 and LiHg . The p values clearly indicate a more chemical nature to the bonding; p ranges from 2.5 to 3.6 (except for Be_2), values far smaller than simple long-range attraction allows. The curvatures are also small, especially for LiHg . These species appear to be incipiently covalent, at least to the extent that one can measure such a concept by the shape of the potential well near R_e . Even though the bond energies are very small, these diatomics are showing the features which dominate the bulk metals and alloys. The alkaline earths are showing the influence of low-lying $nsnp$ and/or $ns(n-1)d$ configurations⁸ (which seem^{3a} to make their influence felt rather abruptly in Be_2 —hence the larger κ value). The anomalously high bond energies of Be_2 and LiHg and their anomalous shape parameters probably cannot be "blamed" on any one factor, but atomic size and unusually low first-excited state energies must play a role.

The Ne-containing rare gas dimers deserve comment. Note the steady increase in κ and p through the series HeNe – NeXe accompanied by a saturation in \mathcal{D}_e at NeAr . As with NaAr , the virial theorem indicates the increasing role of electron kinetic energy rise as Ne contacts larger and larger atoms. Unlike NaAr , however, the electrons on the rare gases are less diffuse; the repulsion is increasingly more abrupt, as reflected by κ and p . The nearly constant bond energies of NeAr – NeXe is somewhat accidental; the regular changes in potential shapes are not.

Finally, we come to one of the outstanding questions posed by Table II. Why is XeF so remarkably different

(33) J. S. Winn, *J. Chem. Phys.*, **74**, 608 (1981).

(34) (a) LiHg : U. Buck, H. O. Hoppe, F. Huiksen, and H. Pauly, *J. Chem. Phys.*, **60**, 4925 (1974); (b) NaHg : U. Buck and H. Pauly, *ibid.*, **51**, 1929 (1971); (c) KHg and CsHg : U. Buck, M. Kick, and H. Pauly, *ibid.*, **56**, 3391 (1972).

Table II
 Potential Well Parameters for Several Weakly Bound Diatomics^a

molecule	D_e	R_e	κ	p	method ^b	ref
He ₂	7.65	2.96	77	5.2	E	d
Ne ₂	29.7	3.03	80	5.6	E	9
Ar ₂	100	3.76	88.4	5.62	ESB	2
Kr ₂	140	4.01	81.4	6.33	ESB	e
	138	4.11	(72-87) ^c	(5-5.6)	E	f
Xe ₂	196	4.36	78.3	6.69	ESB	e
	192	4.45	(88-84)	(5.6-5.5)	E	f
HeNe	9.9	3.21	43	3.64	E	g
HeAr	16.8	3.54	59	4.43	E	g
HeKr	17.2	3.75	57	4.34	E	g
HeXe	17.5	4.15	56	4.29	E	g
NeAr	50	3.43	87	5.60	E	9
NeKr	52	3.58	98	6.00	E	9
NeXe	52	3.75	125	6.91	E	9
Be ₂	800	2.49	59.5	4.94	A	3a,b
Mg ₂	430	3.89	32.7	3.59	S	3a,c
Ca ₂	1095	4.28	41.9	3.56	S	3a,d
Sr ₂	1100	4.50	38	3.35	S	3a,e
NaNe	8.1	5.29	48	4.66	S	11
NaAr	41	4.99	51	4.31	S	10
LiHg	871	3.00	23.5	2.54	E	34a
NaHg	444	4.72	40.9	3.10	E	34b
KHg	420	4.91	40.0	3.00	E	34c
CsHg	403	5.09	46.2	3.40	E	34c
NeF	42	2.85	(110-92)	(6.4-5.8)	E	h
ArF	98	2.95	37.0	3.30	E	h
KrF	108	3.00	37.0	3.30	E	h
XeF	1175	2.32	(144-92)	(7.5-5.8)	E	i
	1175	2.32	116.6	5.53	S	j
XeCl	280	3.23	(54-22)	(4.2-2.3)	E	k
HeNe ⁺	6200	1.33	48.9	4.30	S	16
BeAr ⁺	4536	2.09	27.5	3.16	S	12a,b
BeKr ⁺	5511	2.22	29.1	2.84	S	12a, 13
CaAr ⁺	1000	2.80	36.3	3.93	S	15

^a Energies in cm⁻¹, R_e in Å. ^b Methods: E, elastic scattering; S, optical spectroscopy; B, bulk data used in fit; A, ab initio calculation. ^c If the model potential has two Morse functions joined at R_e , κ and p are not well defined. Data in parentheses list values for the inner Morse function and the outer Morse function, respectively. ^d J. M. Farrar and Y. T. Lee, *J. Chem. Phys.*, **56**, 5801 (1972). ^e J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, *ibid.*, **61**, 3081 (1974). ^f K. K. Docken and T. P. Schafer, *J. Mol. Spectrosc.*, **46**, 454 (1973). ^g C. H. Chen, P. E. Siska, and Y. T. Lee, *J. Chem. Phys.*, **59**, 601 (1973). ^h C. H. Becker, P. Casavecchia, and Y. T. Lee, *ibid.*, **70**, 2986 (1979). ⁱ C. H. Becker, P. Casavecchia, and Y. T. Lee, *ibid.*, **69**, 2377 (1978). ^j D. L. Monts, L. M. Ziurys, S. M. Beck, M. G. Liverman, and R. E. Smalley, *ibid.*, **71**, 4057 (1979). ^k C. H. Becker, J. J. Valentini, D. Casavecchia, S. J. Sibener, and Y. T. Lee, *Chem. Phys. Lett.*, **61**, 1 (1979).

from other rare gas halides? The large curvature implies a very abrupt onset of repulsion. The large well depth and short bond length indicate an important bonding mechanism not available to other rare gas halides. Whether this mechanism can be uniquely identified is not clear.

Concluding Remarks

When two atoms or molecules which would appear to have no great chemical interest in one another are bound to form a weak dimer and when the binding interaction turns out to have properties with periodic variations, or, as with XeF, element-specific surprises, one must look beyond classical electrostatics. The role of electron delocalization in weak bonding may serve to enhance the bonding energy, but an equally valid indicator of delocalization is the change it causes in the shape of the potential well near R_e . The term "delocalization" is used here rather loosely. It is meant to imply those changes in electronic structure that occur in the vicinity of R_e which contribute to binding by reducing the relative rate of increase of the total electron kinetic energy. The curvature of the potential becomes more gentle in such a case (examples are the alkaline earth dimers), which is to be contrasted with,

for instance, the heteronuclear rare gas dimers where the onset of repulsion is much more abrupt.

For polyatomic complexes, the prospects of obtaining details of the entire potential-energy surface are greatly reduced, although considerable progress has been made.³⁵ Even without the detail offered by diatomics, the structural and internal dynamics data on polyatomic complexes show the need for "chemical" language to explain even the grossest features (such as the anisotropy of the weak bond) in certain cases.

It is likely that the precision of language used to describe weakly bound species will sharpen as the body and diversity of data on them grow. We are currently in a transition period. The old rules are known to be insufficient, but the new rules are not yet clearly defined.³⁶ The challenge of finding these rules is an interesting one, since there are $N(N+1)/2$ weakly bound dimers for every N stable compounds! The extension of a small set of rules to such a large body of species (and one should not forget trimers, etc.) is the

(35) See, for instance, J. M. Hutson, A. E. Berton, P. R. R. Langridge-Smith, and B. J. Howard, *Chem. Phys. Lett.*, **73**, 218 (1980), and references therein.

(36) An amusing consequence of our current uncertainty in describing weak bonds is the general lack of a systematic nomenclature for weakly bound species. Should NaAr be considered an "argide" or a "natride"?

intellectual equivalent of, for instance, the concept of sp^3 hybridization to the theory of hydrocarbons.

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1,2-Diazepines: A New Vista in Heterocyclic Chemistry

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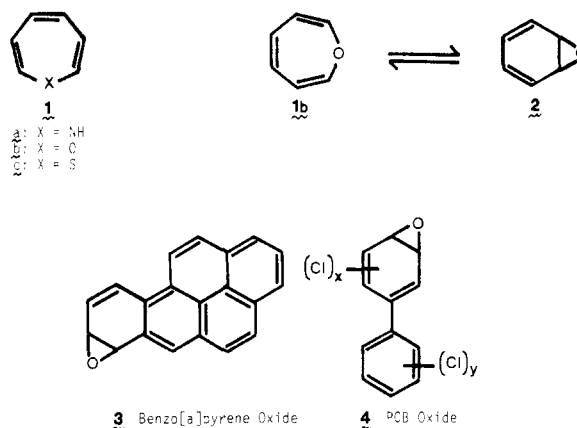
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Chemists have long been familiar with five- and six-membered heteroaromatic substances, e.g., furan, pyrrole, and pyridine, as constituents of petroleum and coal tar and as characteristic structural frameworks of diverse natural products. In contrast, highly unsaturated seven-membered ring heterocycles are of recent, mainly synthetic, origin, and their evolution is linked to advances in theoretical and medicinal chemistry. In the 1960s as part of an intense inquiry into aromatic character, the question of potential antiaromaticity of the 8π -electron systems 1*H*-azepine (1a), oxepin (1b), and thiepin (1c) prompted serious efforts to synthesize these molecules.¹⁻³ Today, only 1c remains for synthetic conquest⁴ while the antiaromaticity question has been in large part answered in the negative on the basis of physicochemical evidence on derivatives of 1a-c^{1,2} and Hückel molecular orbital calculations.⁵ The subsequent demonstration¹ of the oxepin (1b)-oxanorcaradiene (2) equilibrium was instrumental in establishing valence isomerization as a widely encompassing principle in organic chemistry^{6,7} and significantly aided studies in unrelated areas: the mechanism of carcinogenesis of polycyclic aromatic hydrocarbons (3),⁸ the metabolism of environmentally deleterious chemicals (4),⁹ and the biosynthesis of certain natural products.¹⁰

In 1960, while pursuing a trail of structural misassignment, workers at Hoffmann-La Roche discovered the potent sedative and anxiolytic action of certain 1,4-benzodiazepines.¹¹ These findings resulted in a



dominant market position for several therapeutic agents such as Librium (5) and catapulted synthetic activity toward other benzo- and dibenzo-annulated seven-membered-ring heterocycles.¹² Additional stimulus was

(1) Vogel, E.; Günther, H. *Angew. Chem., Int. Ed. Engl.* 1967, 6, 385.
(2) Paquette, L. A. "Nonbenzenoid Aromatics"; Snyder, J. P., Ed.; Academic Press: New York, 1969; Vol. 1, p 249.

(3) Similar incentives catalyzed synthetic work on more unusual 7-membered unsaturated heterocycles of (a) phosphorus [Markl, G.; Schubert, H. *Tetrahedron Lett.* 1970, 1273], (b) silicon [Barton, T. J.; Kippenhan, R. C.; Nelson, A. J. *J. Am. Chem. Soc.* 1974, 96, 2272], and (c) boron [Eisch, J. J.; Galle, J. E. *Ibid.* 1975, 97, 4436].

(4) 1*H*-Azepine (1a) has been recently characterized: Vogel, E.; Altenbach, H.-J.; Drossard, J.-M.; Schmickler, H.; Stegelmeier, H. *Angew. Chem., Int. Ed. Engl.* 1980, 19, 1016. In contrast, only highly substituted thiepins are stable at low temperatures: Reinhoudt, D. N.; Kouwenhoven, C. G. *Tetrahedron* 1974, 30, 2093. Hess, B. A., Jr.; Schaad, L. J.; Reinhoudt, D. N. *Ibid.* 1977, 33, 2685.

(5) Dewar, M. J. S.; Trinajstić, N. *Tetrahedron* 1970, 26, 4269. Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Ibid.* 1972, 28, 3657.

(6) Maier, G. "Valenzisomerisierungen"; Verlag Chemie: Weinheim, 1972.

(7) For valence isomerization of substituted 1*H*- and 4*H*-azepines, see respectively: Prinzbach, H.; Babsch, H.; Fritz, H.; Hug, P. *Tetrahedron Lett.* 1977, 1355. Göckel, U.; Hartmannsgruber, U.; Steigel, A.; Sauer, J. *Ibid.*, 1980, 599.

(8) Gelboin, H., T'so, P., Eds., "Polycyclic Aromatic Hydrocarbons and Cancer"; Academic Press: New York, 1978.

(9) Forgue, S. T.; Preston, B. D.; Hargraves, W. A.; Reich, I. L.; Allen, J. R. *Biochem. Biophys. Res. Commun.* 1979, 91, 475.

(10) Johns, N.; Kirby, G. W. *J. Chem. Soc., Chem. Commun.* 1971, 163.

(11) Sternbach, L. H. *Angew. Chem., Int. Ed. Engl.* 1971, 10, 34. For a personal account, see: Sternbach, L. H. *J. Med. Chem.* 1979, 22, 1.

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