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## The Analysis of AA′BB′ Nuclear Magnetic Resonance Spectra by Weak Double Irradiation. Application to Two Isomeric Cyclobutane Derivatives

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**Abstract:** A general method was developed for the complete analysis of nmr spectra arising from AA′BB′ spin systems. It is based on the weak double irradiation ("tickling") technique and makes it possible to determine unambiguously not only the parameters $\delta_{AB}, J_{AB} + J_{AB'}, J_{AB} - J_{AB'}$, and $J_{AA'} - J_{BB'}$, but also the parameter $J_{AA'} + J_{BB'}$ with its sign relative to those of the others. The method is illustrated by the analysis of spectra of the ring protons of the *cis* and *trans* isomers of 1,2-dibromo-1,2-dicarbomethoxycyclobutane, the preparations of which are described in detail. The vicinal spin coupling constants (${}^3J_{HH}$'s) between equivalent protons ($J_{AA'}$ and $J_{BB'}$) alone allow one to distinguish between the *cis* and the *trans* isomers, a result which was confirmed chemically and by X-ray diffraction.

The analysis of AA′BB′ spectra has been a matter of considerable study,[1] because the frequently occurring AA′BB′ system gives rise to a symmetrical spectrum in which the positions of only 2 × 6 of up to 2 × 12 observable lines can easily be expressed in closed form. Although the position of the other lines can be written in terms of the roots of a quartic equation, their algebraic manipulation is too cumbersome to be useful in practice.

Thus a complete analysis of an AA′BB′ spectrum is usually made by trial and error: a set of values for $\delta_{AB} \equiv \delta$, $N = J_{AB} + J_{AB'}$, $L = J_{AB} - J_{AB'}$, and $M = J_{AA'} - J_{BB'}$ is found from lines assumed to be those derivable from algebraic expressions,[2] and spectra are computed for various values of $K = J_{AA'} + J_{BB'}$, until a satisfactory match is obtained. One drawback of this procedure is that the assignment of lines from which parameters $\delta$, $N$, $L$, and $M$ are determined may not be unambiguous. Furthermore, a final decision on the correctness of the parameters often cannot be made on spectral grounds alone, as several sets of parameters may yield computed spectra in equally good agreement with the experimental one. Thus, "reasonableness" of parameters must be invoked, for instance, in the case of *o*-dichlorobenzene.[3] For certain classes of molecules such as disubstituted benzenes[4] or 1,2-disubstituted ethanes,[5,6] trends observed in the spectra, produced by changes in the parameters, have been helpful in the assignment of lines. But the multitude of combinations for the five parameters $\delta$, $N$, $L$, $K$, and $M$ precludes a general treatment of the AA′BB′ system on the basis of trends in spectral correlations.[7]

The method outlined below is based on the fact that a complete and unique energy level diagram (ELD) for the AA′BB′ system can be built up from the spectrum with the aid of weak double irradiation experiments ("tickling"),[8] and that such a diagram yields the value of $K$.

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[1] See P. L. Corio, *Chem. Rev.*, **60**, 363 (1960); "Structure of High-Resolution NMR Spectra," Academic Press Inc., New York, N. Y., 1966, pp 376–384.

[2] B. Dischler, *Z. Naturforsch.*, **20a**, 888 (1965).

[3] D. R. Whitman, *J. Chem. Phys.*, **36**, 2085 (1962).

[4] D. M. Grant, R. C. Hirst, and H. S. Gutowsky, *ibid.*, **38**, 370 (1963).

[5] R. J. Abraham and K. G. R. Pachler, *Mol. Phys.*, **7**, 165 (1963).

[6] R. C. Hirst and D. M. Grant, *J. Chem. Phys.*, **40**, 1909 (1964).

[7] K. B. Wibert and B. J. Nist, "The Interpretation of NMR Spectra," W. A. Benjamin, Inc., New York, N. Y., 1962, pp 309–317.

[8] R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

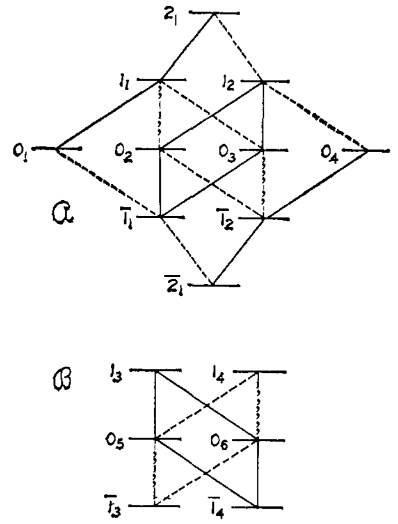

Figure 1. Energy level diagram for the AA'BB' system: transitions in high-field half, solid lines; in low-field half, broken lines. Only $|2_1|-|1_{1,2}|$ transitions can be predicted to occur in the low- or the high-field half of the spectrum. In this diagram, the marking of the other transitions as to their occurrence in one or the other half of the spectrum is only illustrative for the $\mathcal{A}$ species. See, *e.g.*, Figure 2b for a different situation. The $\mathcal{A}$ diagram can always be drawn in the way indicated here.

The essential features of the tickling experiment are: (1) application of a second radiofrequency field $H_2$ at the frequency of a line $\nu_a$; (2) splitting of lines $\nu_k$, which have an energy level in common with line $\nu_a$, into two components; (3) provided that the frequency of $H_2$ is set exactly at $\nu_a$, the splitting will be symmetrical and (a) well resolved if the transitions involving lines $\nu_a$ and $\nu_k$ span an interval $\Delta m = 1$ ("regressive pair" of transitions), or (b) poorly resolved if the transitions span an interval $\Delta m = 2$ ("progressive pair").

These features allow one not only to construct ELD's through connection relations of transitions, but also to sort out transitions belonging to different symmetry species, or lines which arise from spin systems other than those under study. (Actually the optimum tickling frequency is $\nu_a + \Delta\nu_a$, but for most practical purposes, $\Delta\nu_a$ is negligibly small.[8])

**Analysis of an AA'BB' Spectrum from Its Energy Level Diagram.** The expressions for the energy levels and the corresponding diagrams as well as those for the transitions and their intensities have been given by various authors.[2,3] The diagram for the $\mathcal{A}$ species can always be depicted in the manner shown in Figure 1, which is the most symmetrical form with the least number of lines crossing each other, and thus most convenient for the building up of an ELD from tickling experiments. The energy levels are labeled by $F_z$ ($F_z = +2, +1, 0, -\bar{1}$, and $-\bar{2}$) and designated $2_i$, $1_i$, $0_i$, $\bar{1}_i$, and $\bar{2}_i$, respectively, where $i$ is a running number. Frequencies are labeled by subscripts denoting the energy levels between which the corresponding transitions take place.

If the quantity $^1/_2N + {}^1/_4K$ is subtracted from all diagonal elements in the Hamiltonian matrices for the $\mathcal{A}$ species and the Larmor frequencies of the A and B nuclei are referred to the center of the AA'BB' band so that $\omega_A + \omega_B = 0$, the eigenvalue (energy level) with $F_z = +2$ becomes equal to that with $F_z = -2$, and the same is true for the set of levels with $F_z = +1$ and $F_z = -1$. The resulting shift of all energy levels, which of course leaves the spectrum unchanged, gives a clearer picture of their relative positions. It should also be noted that in the $\mathcal{B}$ group no such relationships can be brought out.

With this convention the group of 1–0 and 0–$\bar{1}$ transitions has the exclusive property that for each of its six pairs the relationship holds that $\nu_{1_i-0_j} = -\nu_{0_j-\bar{1}_i}$. This has two important consequences for the interpretation of results of tickling experiments. (1) If a line $\nu_k$ is tickled and a line $-\nu_k$ is affected, both belong to the $\mathcal{A}$ group and are 0–$|1|$ transitions; the lines $\nu_k$ and $-\nu_k$ are necessarily a progressive pair. (2) If any of these $\nu_{0-|1|}$ lines is tickled and a line that is not a $\nu_{0-|1|}$ line is affected, it is a $|2|-|1|$ transition. Such pairs, $\nu_{0-|1|}$ and $\nu_{|2|-|1|}$, are also progressive. In this manner all $\mathcal{A}$ lines are identified. The remaining lines are necessarily $\mathcal{B}$ lines.

0–$|1|$ transitions are further classified into those which involve energy levels $0_1$ and $0_4$, and $0_2$ and $0_3$. $0_1$ and $0_4$ lines have energy levels in common with only four other lines, whereas $0_2$ and $0_3$ lines share energy levels with six other lines. Once a distinction has been made between these two types of 0–$|1|$ lines by a tally of affected lines, the complete energy level diagram of the $\mathcal{A}$ species can be constructed. This process is aided by (see Figure 1) (1) sum relations such as $\nu_{1_1-0_2} + \nu_{0_2-\bar{1}_2} = \nu_{1_1-0_3} + \nu_{0_3-\bar{1}_2}$, (2) the fact that the $2_1$–$1_1$ and $2_1$–$1_2$ lines belong to different halves of the AA'BB' spectrum (the same is true for the $\bar{2}_1$–$\bar{1}_i$ lines), and (3) the progressive or regressive character of line pairs. Consideration 3 is very helpful, but not indispensable for the building up of the ELD of the $\mathcal{A}$ group.

In actual practice, one would start evaluating the tickling results by drawing the $|2|-|1|$ transitions in the ELD together with those involving $0_1$ and $0_4$. The labeling of the other two 0 transitions is immaterial, as long as the above-mentioned sum relations are obeyed. Now the level $2_1$ is arbitrarily given the value zero,[3] and the energy levels are calculated as referred to level $2_1$. With this convention, the relation $K = 3(1_1 + 1_2) - (0_1 + 0_2 + 0_3 + 0_4)$, derived by Whitman,[3] allows the hitherto elusive parameter $K$ to be determined directly from experiment. The ELD also yields $\delta$ and $N$, either by application of Whitman's relations or by those given by Dischler.[2]

The parameters $L$ and $M$ (and again $\delta$) can be calculated in the known manner[2] from the $\mathcal{B}$ lines, since these have been assigned unambiguously. Further confirmation of these assignments can be obtained from a consideration of tickling results predictable from the ELD of the $\mathcal{B}$ group (see Figure 1).

The sign of $K$ relative to $N$ is not directly accessible either from the spectrum or from the ELD built up through tickling experiments, because the sign of $N$ involves the ambiguity of a square root.[2]

For a strongly coupled AA'BB' system (relatively small $\delta$), such as that arising from the *cis* isomer, the magnitude and sign of $K$ can be found by computation of trial spectra as indicated above, because the lines depending on $K$ change position and intensity with variations of $K$. However, in relatively weakly coupled systems (large $\delta$), the spectrum becomes rather insensitive to the relative signs of $N$ and $K$, that is, to those of $J_{AB}$ and $J_{AB'}$ and of $J_{AA'}$ and $J_{BB'}$. This is the case for

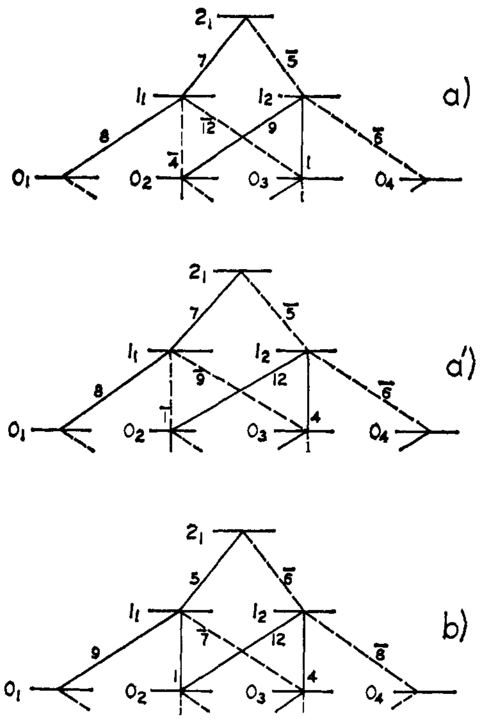

Figure 2. Energy level diagrams for the $\mathfrak{a}$ species of AA′BB′ systems in 1,2-dibromo-1,2-dicarbomethoxycyclobutanes ($\omega_0$ = 100 MHz): (a) for the *trans* isomer, as established by tickling with $N = \pm 4.13$ Hz, $K = \pm 12.57$ Hz; sign of $K$ relative to that of $N$ from computed ELD (see Tables I and II); (a′) same, but computed for $N = +4.13$ Hz and $K = \pm 12.57$ Hz; in disagreement with results from tickling experiments (see Table I); (b) for the *cis* isomer, as established by tickling with the sign of $K$ relative to that of $N$ from computed spectrum and energy level diagram (see Tables I and II); transitions in high-field half, solid lines; in low-field half, broken lines. Energy levels $\bar{1}_1$, $\bar{1}_2$, and $\bar{2}_1$ (and transitions thereto) are omitted, as they are equal to $1_1$, $1_2$, and $2_1$. The numbering of lines (1, 2, ..., $\bar{1}$, $\bar{2}$, ...) follows the observed sequence, starting from the center of the AA′BB′ spectra (see Figure 4), and stands for the line frequencies $\nu_1, \nu_2, \ldots, -\nu_1, -\nu_2\ldots$

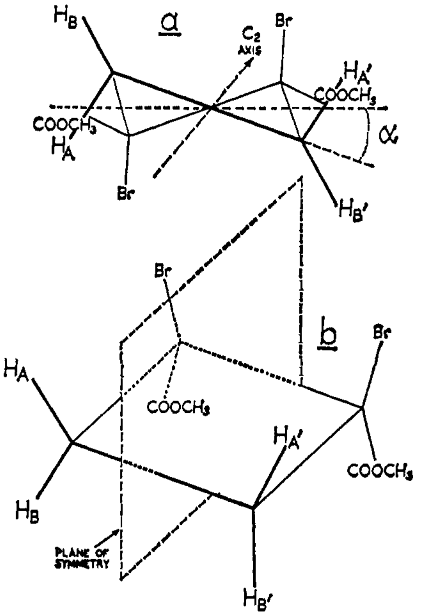

Figure 3. Geometry of 1,2-dibromo-1,2-dicarbomethoxycyclobutanes: a, *trans* isomer; b, *cis* isomer; α, angle of twist with respect to a planar cyclobutane ring.

the *trans* isomer, where such a change in signs produces a maximum shift of about 0.1 Hz in only two lines (for $\omega_0$ = 100 MHz). Thus, even if the observed spectrum were fitted by an iterative procedure, it would be difficult to distinguish between the two cases of relative signs of $K$ through the magnitude of the root-mean-square error.

However, the ELD's for the cases of $K$ positive and $K$ negative are different with regard to connections of 0–|1| lines (see Figure 2). To decide which of the two likely schemes gives rise to the spectrum under study, we used the magnitudes of $\delta$, $N$, $L$, $K$, and $M$ to compute the energy levels for $+K$ and $-K$ (with respect to $N$), constructed the two ELD's, and compared them with the scheme built up with the aid of tickling experiments (see Tables I and II and Figure 2). Only the ELD of Figure 2a agreed with the tickling results (see Table I).

We must emphasize that in the analysis of AA′BB′ spectra by the present method, a computer is needed only for the determination of the sign of $K$, but not for any trial-and-error fitting of an experimental spectrum, except perhaps for a final refinement of parameters.

***cis*- and *trans*-1,2,-Dibromo-1,2-dicarbomethoxycyclobutane.** In order to illustrate the method outlined above, we chose the two title molecules (see Figure 3), whose spectra are of interest for the following reasons. (1) Their 100-MHz spectra (Figure 4) show all or most of the 2 × 12 expected lines resolved, which makes for a rather straightforward interpretation of the tickling results. (2) In this pair of *cis-trans* isomers, the spectrum of one of them had been analyzed previously,[9] but only through a trial-and-error fit with computed spectra. It therefore seemed desirable to check that analysis by the present reliable method. In particular, the conclusions drawn on relative signs of $^2J_{HH}$ and $^3J_{HH}$ require an unambiguous analysis of the spectra.

**Table I.** Results from Tickling Experiments[a]

TICKLED LINES

For *trans* Compound (AFFECTED LINES by TICKLED LINES)

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $\bar{1}$ | P | | | | P | R | | | | | | R |
| $\bar{2}$ | | | P | | | | | | | R | | |
| $\bar{3}$ | | P | | | | | | | | | R | |
| $\bar{4}$ | | | | P | | | P | R | R | | | |
| $\bar{5}$ | P | | | | | | R | | P | | | |
| $\bar{6}$ | R | | | | | P | | | R | | | |
| $\bar{7}$ | | | | P | R | | | | | | | P |
| $\bar{8}$ | | | | R | | | | P | | | | R |
| $\bar{9}$ | | | | R | P | R | | | P | | | |
| $\bar{10}$ | | R | | | | | | | | | P | |
| $\bar{11}$ | | | R | | | | | | | P | | |
| $\bar{12}$ | R | | | | | | P | R | | | | P |
| 1 | | | | | | | | | R | | | P |
| 2 | | | | | | | | | | R | P | |
| 3 | | | | | | | | | | P | R | |
| 4 | | | | | | | | | P | | | R |
| 5 | | | | | | P | | | | | | |
| 6 | | | | | P | | | | | | | |
| 7 | | | | | | | | P | | | | |
| 8 | | | | | | | P | | | | | |
| 9 | R | | | P | | | | | | | | |
| 10 | | R | P | | | | | | | | | |
| 11 | | P | R | | | | | | | | | |
| 12 | P | | | R | | | | | | | | |

For *cis* Compound

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8+9 | 10 | 11 | 12 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\bar{1}$ | P | | | | | | R | | | | |
| $\bar{2}$ | | | | | | | | | | | |
| $\bar{3}$ | | | | | | | | | | | |
| $\bar{4}$ | | | | P | | | R | R | | | |
| $\bar{5}$ | | | | | | | P | | | | |
| $\bar{6}$ | | | | P | R | | | | | | |
| $\bar{7}$ | R | | | R | P | | P | R | | | |
| $\bar{8}+\bar{9}$ | | | | R | | | R | P | | | |
| $\bar{10}$ | | R | P | | | | | | | | |
| $\bar{11}$ | | P | R | | | | | | | | |
| $\bar{12}$ | P | | | | | | | R | | | |
| 1 | | | | | P | | | R | | | |
| 2 | | | | | | | | | | | |
| 3 | | | | | | | | | | | |
| 4 | | | | | | | P | | | | |
| 5 | P | | | | | | | P | | | |
| 6 | | | | | | | | P | | | |
| ·7 | | | | P | | | | | | | |
| 8+9 | R | | | | P | | | | | | |
| 10 | | R | | | | | | | | | |
| 11 | | | R | | | | | | | | |
| 12 | R | | | R | | | | | | | |

[a] Connections between tickled and affected lines: R, regressive; P, progressive. Connections not shown, though expected from the ELD's (see Figure 2), could not be established experimentally.

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(9) E. Lustig, *J. Chem. Phys.*, 37, 2725 (1962).

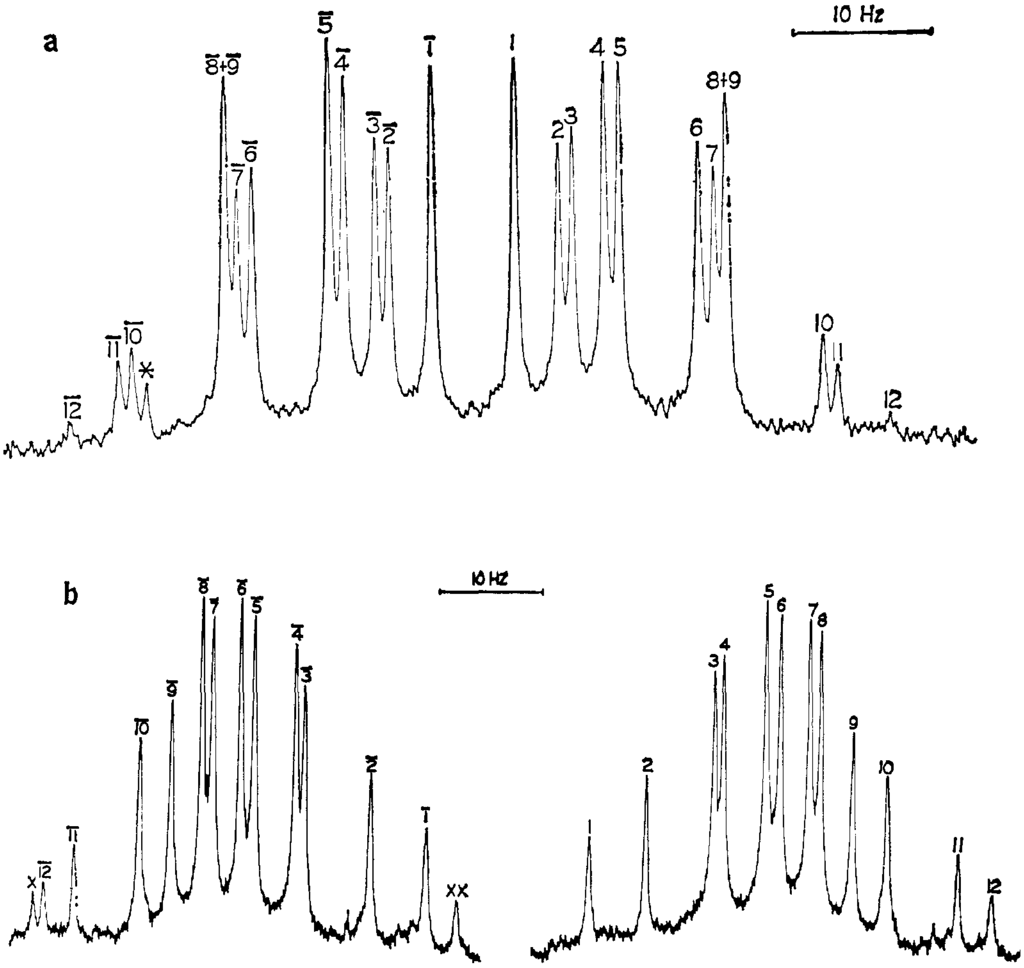

Figure 4. 100-MHz spectra of AA′BB′ bands of 1,2-dibromo-1,2-dicarbomethoxycyclobutanes; sweep rate, 0.1 Hz/sec; frequency sweep: (a) *cis* isomer: *, extraneous peak; (b) *trans* isomer: x, spinning side-band peak from -COOCH$_3$; xx, extraneous peak.

(3) The magnitude of the $^3J_{HH}$'s may give a clue as to whether one or the other isomer is *cis* or *trans*. That $^3J_{HH}$'s are indicative of the configuration of a four-membered ring was recently shown.[10]

**Table II.** Energy Levels for $\mathfrak{a}$ Lines (Hz)[a]

| | *cis* | *trans* |
|---|---|---|
| $1_1$ | 16.44 | 51.67 |
| $1_2$ | −10.67 | −47.48 |
| $0_1$ | 34.85 | 104.12 |
| $0_2$ | 6.88 | 8.35 |
| $0_3$ | −13.74 | −17.12 |
| $0_4$ | 29.08 | −96.33 |

[a] $2_1$ was set arbitrarily at zero, and the weaker of the $|2_1|-|1_i|$ transitions was positive; $\omega_0$ = 100 MHz.

The results of the analysis of early spectra, carried out before X-ray data[11] were available, strongly suggested that the molecule with $\delta = 99.3$ Hz was the *trans* isomer and that with $\delta = 25.1$ Hz was the *cis* isomer. The significance of this finding will be discussed below.

## Results and Discussion

The results of the tickling experiments are summarized in Table I. The energy levels for the $\mathfrak{a}$ species are given in Table II, and their connection in the ELD's is shown in Figure 2. The parameters of the AA′BB′ spectra are collected in Table III. All numerical data reported are derived from "averaged" spectra. For 100-MHz spectra, see Figure 4.

Observed and computed 60-MHz spectra (based on parameters obtained at 100 MHz) showed an average deviation of 0.1 Hz per line (0.12 Hz for the *trans* and 0.08 Hz for the *cis* compound). The smallness of this deviation, which is within experimental error, corroborates the correctness of the parameters.

The chemical shifts of the A and B protons are $\tau$ 7.658 and 6.658 for the *trans* and $\tau$ 7.436 and 7.172 for the *cis* compound (from Table III, column *d*).

**A. Construction of ELD's from Tickling Experiments.** The tickling experiments with the *trans* isomer could be readily performed and interpreted in accordance with the reasoning described above, because all 2 × 12 lines were resolved. A further reason for our being able to derive useful information from tickling *all* lines was that they are sufficiently intense and, in particular, that the weaker lines are well separated from each other. Thus, no excessive amount of power (H$_2$) was needed in their irradiation to split other lines.

The reasoning leading to the construction of the ELD for the *cis* isomer (Figure 2b) is given below in detail, because it illustrates two somewhat complicating situations which may often occur: weak lines and lines very close to each other or coincident.

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[10] E. Lustig and R. M. Moriarty, *J. Am. Chem. Soc.*, **87**, 3252 (1965).

[11] I. L. Karle, J. Karle, and K. Britts, *ibid.*, **88**, 2918 (1966).

In the case of the *cis* compound, the lines[12] |10|, |11|, and |12| were so weak, and the lines of the pair |10| and |11|, in addition, so close to each other, that an $H_2$ applied to them and strong enough to split other lines "spilled over" to other than the one just irradiated and thus made for an unclear pattern of affected lines. We therefore entirely omitted reporting on the results of the tickling of lines |10|, |11|, and |12|.

Since tickling of *both* lines of a pair $\nu_i$ and $\nu_j$ (connected or not) merely confirms the result of tickling one of them, say, $\nu_i$, the result from tickling line $\nu_j$ does not yield any new information regarding their connection. Thus the diagram of Table Ib contained enough clues to enable us to build the ELD's of the $\mathcal{A}$ and $\mathcal{B}$ species.

Lines |2|, |3|, |10|, and |11| on the one hand, and the remaining lines on the other, form two separate sets not connected with each other. The fact that in the first set only four lines occur marks them as the $\mathcal{B}$ lines. Moreover, in no case where any of these lines, say, $\nu_i$, was tickled was a line $-\nu_i$ perturbed or found to be connected with other lines $\nu_k$ connected with lines $-\nu_k$. Thus lines |2|, |3|, |10|, and |11| are definitely not $\mathcal{A}$ lines.

In the $\mathcal{A}$ group, only four and not six peaks $\nu_i$ show splitting of the "mirror" line $-\nu_i$. This is plausible: not all of the $\mathcal{A}$ lines were tickled (|12| was left out; see above), and the peak denoted |8 + 9| is obviously a composite of two lines, since tickling it produced splitting of more than six lines.[13] It is then clear from Table Ib (*cis* compound) that of the lines |1|, |4|, |5|, |6|, |7|, |8 + 9|, and |12| the lines |1|, |4|, |7|, |8|, |9|, and |12| are transitions between energy levels $1_i$ and $0_j$.

That |12| also belongs to this group is borne out by the fact that tickling 1 produces a perturbation in |12| *and* $|\overline{12}|$. The observations that both lines of a "mirror" pair of the $\mathcal{A}$ group are perturbed by tickling of a third line, and inspection of the general ELD (Figure 1), show that lines of such a mirror pair not only are $1_i$–$0_j$ transitions but also that $j = 2$ or 3. This applies to lines |12| and also to lines |4| and |7|. The assignment of |4| and |7| to $|1_i|$–$|0_{2,3}|$ transition is further confirmed by the fact that tickling them produces splitting in six lines. These special considerations, in addition to the general ones mentioned above sufficed to buildup the ELD of the $\mathcal{A}$ group as shown in Figure 2a.

**B. Nmr Parameters and Structure of the Two Molecules.** The nmr spectra of the four ring protons of both molecules are of the AA'BB' type; that is, two resonance frequencies and four spin coupling constants are sufficient to describe the spectra so well that the root-mean-square errors in fitting and the probable errors of the parameters lie well within experimental errors. The twofold symmetry necessary for these systems to be of the AA'BB' type is dependent on both the structure of the molecule and the nature of the ring-puckering motion in the case of the *cis* molecule and only on the structure in the case of the *trans* molecule.

The potential function for the out-of-plane bending vibration for the *cis* molecule is symmetrical about a planar configuration with the result that the two A protons are rapidly exchanging between two environments producing a single chemical shift $\omega_A$, and likewise the rapid exchange rate between the two B protons yields a single chemical shift $\omega_B$. Similarly, the two *trans* $^3J_{HH}$ pairs, AB' and A'B, exchange rapidly between the two environments corresponding to the two indistinguishable conformations of the molecule with the result that only the average *trans*-$^3J_{HH}$ is observed. The ensuing situation therefore gives rise to an AA'BB' spectrum and is equivalent to treating the molecule as possessing $C_s$ symmetry.

The *trans* molecule should have a skewed potential function for its out-of-plane bending vibration. However, this molecule, irrespective of the nature of this potential function, possesses $C_2$ symmetry and consequently has an AA'BB' spectrum, whereas the *cis* molecule gives an AA'BB' spectrum only as a result of its out-of-plane bending vibration being symmetric about the plane of the ring.

The original problem was to distinguish between the *cis* and *trans* molecules on the basis of their nmr spectra. Since $|J_{AA'} - J_{BB'}| = 6.89$ Hz for one molecule and $|J_{AA'} - J_{BB'}| = 1.25$ Hz for the other molecule and since $J_{AA'}$ and $J_{BB'}$ must be either both *cis*-$^3J_{HH}$'s or both *trans*-$^3J_{HH}$'s, we predicted that the smaller value of $|J_{AA'} - J_{BB'}|$ should correspond to the *cis* molecule. This prediction was made on the basis that the $^3J_{HH}$'s are angle dependent and that substituent effects on $^3J_{HH}$'s are usually small (*ca.* 1–2 Hz). Because of the symmetrical nature of the out-of-plane bending vibration for the *cis* molecule, both $^3J_{HH}$'s should be a measure of the (identical) dihedral angles, and their difference should reflect only different substituent effects, thereby yielding a small value for $|J_{AA'} - J_{BB'}|$. This reasoning was used before in deciding on the *cis–trans* isomerism in the cyclobutane ring of anemonin;[10] there the conspicuously large $|J_{AA'} - J_{BB'}|$ pointed to *trans* isomerism, which was confirmed by X-ray data.[14]

Our prediction was substantiated by a chemical test. Bromine could be eliminated by ethanolic NaI to yield the corresponding cyclobutene 7 only from the isomer with $|J_{AA'} - J_{BB'}| = 6.89$ Hz, but not from that with $|J_{AA'} - J_{BB'}| = 1.25$ Hz (see Experimental Section). This reaction is known to occur only with bromines in the *trans* position.[15] The definitive proof of the proposed identity of the two isomers was finally furnished by complete structure determinations of both isomers through X-ray diffraction.[11]

Some further comments are in order. (1) As one can see from Table III, in each of these AA'BB' systems only one $J$ appears whose sign differs from that of the other three $J$'s; it is a $J$ between two nonequivalent protons (see Figure 3) in each case. These facts, together with a consideration of their magnitudes, suggest that these $J$'s are $^2J_{HH}$'s. In accordance with current theory and experimental results,[16] we gave this $J$ a negative sign and related the signs of the other $J$'s to it. (2) The compound dealt with in a paper[9] on relative

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[12] Where vertical bars are used to denote lines $\nu_k \equiv |k|$, both lines $+\nu_k$ and $-\nu_k$ are meant.

[13] This assumption is justified for two more reasons. (a) In the $CDCl_3$ solution, where $\delta$ differs by about 1.5 Hz from $\delta$ in the $CS_2$ solution (see Experimental Section and Table III, columns *b* and *d*) lines |8| and |9| were found to be separated by 0.9 Hz. (b) As computed spectra for $^1/_2\delta = 13.23$ Hz show, the positions of lines |8| and |9| differ by 0.06 Hz, which is on the limit of the resolving power of the HA-100.

[14] R. M. Moriarty, C. R. Romain, I. L. Karle, and J. Karle, *J. Am. Chem. Soc.*, 87, 3251 (1965).

[15] See W. Hückel, W. Tappe, and G. Legutke, *Ann.*, **543**, 191 (1960).

[16] A. A. Bothner-By and J. A. Pople, *J. Chem. Phys.*, **42**, 1339 (1965).

**Table III.** Nmr Parameters of *trans*- and *cis*-1,2-Dibromo-1,2,dicarbomethoxycyclobutane[a]

| | *trans* | | | *cis* | | | |
|---|---|---|---|---|---|---|---|
| | *b* | *c* | *d* | *b* | *c* | *d* | *e* |
| $^1/_2\delta$ | 49.63 | 49.50 | 49.53 [0.03] | 12.54 | 13.25 | 13.23 [0.06] | 12.8 |
| $N$ | −4.32 | 4.25 | (−4.99) | −5.78 | 5.78 | (−5.73) | −5.8 |
| $L$ | −22.18 | 22.19 | (−22.20) | −19.30 | 19.22 | (+19.19) | 18.2 |
| $K$ | +13.38 | 13.17 | (+13.18) | +18.15 | 18.40 | (+18.29) | 18.4 |
| $M$ | +6.89 | 6.74 | (+6.74) | +1.25 | 1.19 | (+1.20) | 1.6 |
| $J_{AB}$ | −13.25 | −13.17 | −13.19 [0.04] | −12.54 | −12.49 | −12.46 [0.11] | −12.0 |
| $J_{AB'}$ | +8.93 | +8.97 | +9.00 [0.06] | +6.76 | +6.72 | +6.73 [0.08] | +6.2 |
| $J_{AA'}$ | +10.13 | +10.00 | +10.01 [0.06] | +9.70 | +9.89 | +9.75 [0.13] | +10.0 |
| $J_{BB'}$ | +3.24 | +3.26 | +3.27 [0.05] | +8.45 | +8.61 | +8.55 [0.18] | +8.4 |
| $\epsilon_n$ | $\epsilon_4 = 0.021$ | | $\epsilon_2 = 0.009$ | $\epsilon_9 = 0.033$ | | $\epsilon_2 = 0.033$ | |

[a] For proton AA′BB′ band; values in Hz; $\omega_0$ = 100 MHz; $\epsilon_n$ = root-mean-square error after *n* iterations; values in parentheses are derived from the *J*'s below ($J_{AB}$, etc.); values in brackets are probable errors. [b] From direct analysis of early spectra. *K* by trial and error. Values from iteration with LAOCOON II.[17] [c] Latest work (with the aid of tickling). Signs of $J_{AA'}$ and $J_{BB'}$ relative to those of $J_{AB}$ and $J_{AB'}$ from computed energy level scheme (see Figure 4). [d] Latest work (with the aid of tickling). Values refined by LAOCOON II. [e] From ref 9. The value $^1/_2\delta$ = 12.8 Hz was converted from the actual $^1/_2\delta$ = 7.7 Hz obtained at $\omega_0$ = 60 MHz.

signs of $J_{HH}$'s must have been the *cis* and not the *trans* isomer. Mislabeling of the sample vial may have caused this confusion. At any rate, the conclusions reached in that note are not affected by this and are confirmed by the present work (see previous paragraph).

## Experimental Section

**Nmr Spectroscopy.** The 100-MHz spectra were taken on Varian HA-100 spectrometers, operating in the frequency sweep mode, and the 60-MHz spectra on a Varian A-60 spectrometer. Tickling experiments were carried out in the frequency sweep mode with an HA-100 and with the aid of a Hewlett-Packard 200 CD audio oscillator and a Hewlett-Packard 5512A electronic frequency counter. Fine control of the frequency setting of the 200 CD was achieved by a ten-turn 5-kohms variable resistor inserted between the condenser C5C and the tie point of the resistors R6 through R10. The stability of the audio oscillators involved, those of the V-4354 field-frequency stabilization unit of the HA-100 and the 200 CD, were monitored with the frequency counter and found to vary by less than 0.01 Hz over 15-min spans.

Early spectra were recorded with $CDCl_3$ solutions, and line positions were taken directly from precalibrated charts. Spectroscopy performed in connection with the tickling experiments was done on a $CDCl_3$ solution of the *trans* and a $CS_2$ solution of the *cis* isomer. All solutions were about 25% weight per volume and were vacuum degassed. The preparation of the compounds is described in the next section.

Since nonlinearities in the sweep circuitry used for chart presentation of spectra cause slight inaccuracies in the display of peaks, the position of each individual peak was measured by multiple period averaging. In this way peak positions could be measured to about 0.03 Hz.

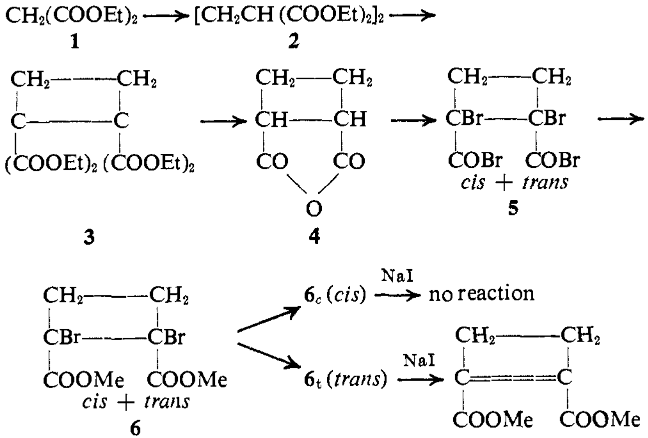
Even though the data listed in Tables II and III are reported to 0.01 Hz, they are reliable only to 0.03 Hz. This is due to the inherent uncertainty of the measurements, caused by noise, finite pen width, and slight instabilities of the spectrometer. Peak positions are not necessarily line positions, because of overlap of lines of finite width. All these factors contribute to the root-mean-square errors of the fitted spectra (see Table III); since overlap of wings is more severe in the spectrum of the *cis* than in that of the *trans* compound (see Figure 4), the fact that the root-mean-square error for the *cis* compound is about three times as large as for the *trans* compound may be attributed in part to overlap.

The peak positions used for the calculations of the energy levels and spectral parameters and for fitting by computer were in one case those actually measured and in the other case those "averaged," so that $|\nu_i| = |-\nu_i|$, as was done by Whitman.[3] When actually measured peak positions were used, the root-mean-square errors were 0.070 Hz for the *cis* and 0.036 Hz for the *trans* compound; the corresponding nmr parameters differed only slightly from those reported for the "averaged" spectra in column *c* of Table III.

In the tickling experiments, $\omega_2$ was adjusted to produce a doublet pattern for the affected lines. Then $H_2$ was set, through the output voltage control of the 200 CD, to create significant differences in the resolution of the doublet splitting. These steps were repeated several times, so that as neat as possible a differentiation was obtained of the character of line connections, that is, a clear distinction between progressive and regressive pairs. Once the optimum values of $\omega_2$ and $H_2$ had been established for each line to be tickled, spurious effects such as beat patterns and distortions of other lines, which otherwise did occur, disappeared. In the present work no attempt was made to calibrate $H_2$ in terms of the output settings of the 200 CD.

The program LAOCOON II[17] was used to calculate spectra and refine parameters and to compute energy levels through appropriate snapshots.

**Preparations.** The two isomeric 1,2-dibromo-1,2-dicarbomethoxycyclobutanes were prepared by the following sequence of reactions.



**Tetraethyl 1,1,2,2-Cyclobutanetetracarboxylate (3).** Tetraethyl 1,1,4,4-butanetetracarboxylate (2) was prepared by the procedure of Golomov and Malevannaya, with diethyl malonate (1) as starting material. The cyclization of 2 was carried out as follows.

To a solution of 22.1 g (0.96 g-atom) of sodium in 500 ml of absolute ethanol was added 165.0 g (0.48 mole) of tetraethyl 1,1,4,4-butanetetracarboxylate. After the resulting yellow-green solution was stirred in an ice bath for 30 min, 76.7 g (0.48 mole) of bromine was added over a 2.5-hr period. The reaction mixture was allowed to warm to room temperature overnight and then added to cracked ice. The layers were separated, and the aqueous phase was extracted with six 200-ml portions of ether. The ether extracts and the original organic layer were combined, washed with two 250-ml portions of water, and dried over anhydrous magnesium sulfate. Removal of the ether under reduced pressure and fractionation of the residue through a 2-in. short-path column gave 131.5 g (80%) of tetraethyl 1,1,2,2-cyclobutanetetracarboxylate (3), bp 123-126°, $n^{25}\text{D}$ 1.4488 [lit.[18] bp 148-150° (1 mm), $n^{20}\text{D}$ 1.4509].

***cis*-Cyclobutane-1,2-dicarboxylic Anhydride (4).** Tetraethyl 1,1,-

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(17) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(18) V. P. Golmov and Z. P. Malevannaya, *J. Gen. Chem. USSR*, **31**, 665 (1961).

2,2-cyclobutanetetracarboxylate (**3**) (125.5 g, 0.36 mole) was converted to 15.5 g (36% yield) of *cis*-cyclobutane-1,2-dicarboxylic anhydride (**4**), as described in the literature,[18–20] bp 102–104° (1.1 mm), mp 76–78° [lit.[18] bp 113–114° (2 mm), mp 78°].

***cis*- and *trans*-1,2-Dibromocyclobutane-1,2-dicarbonyl Bromide (5).** A modification of the methods of Perkin[19] and Kipping and Wren[21] was used to prepare *cis*- and *trans*-1,2-dibromocyclobutane-1,2-dicarbonyl bromide (**5**). To a mixture of 12.6 g (0.10 mole) of cyclobutane-1,2-dicarboxylic anhydride (**4**) and 20 ml (0.20 mole) of phosphorus tribromide, which had been stirred for 15 min, was added 30 ml (0.42 mole) of dry bromine over a 25-min period. The addition of bromine was accompanied by an evolution of heat and the precipitation of phosphorus pentabromide. After the mixture was heated at 85–90° for 2 hr, 5 ml of bromine was added and the heating continued for 16 hr. An additional 1 ml of bromine was then added and the heating at 85–90° continued for 2 hr more. The reaction mixture was then cooled to room temperature, during which time nitrogen was bubbled in to remove part of the unreacted bromine, and extracted with two 40-ml portions of benzene. The benzene extracts were shaken with 150 ml of ice water; the aqueous phase was separated and extracted with two 25-ml portions of benzene, and the combined benzene extracts were dried over anhydrous sodium sulfate. The benzene was removed under reduced pressure and the pale yellow liquid which remained was distilled through a 2-in. short-path distillation column to yield 37.6 g (80%) of *cis*- and *trans*-1,2-dibromocyclobutane-1,2-dicarbonyl bromide (**5**), bp 98–100° (0.08 mm) [lit.[21] bp 104–117° (0.4 mm)].

***cis*- and *trans*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane (6).** The *cis*- and *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutanes (**6**) were prepared and separated according to a variation of the method reported by Kipping and Wren.[21]

To a stirred solution of 4.2 ml (0.04 mole) of N,N-dimethyl aniline, 25 ml of anhydrous methanol, and 15 ml of anhydrous ether was added, over a 0.5-hr period, a solution of *cis*- and *trans*-1,2-dibromocyclobutane-1,2-dicarbonyl bromides (**5**) in 5 ml of dry ether. During the addition, refluxing of the ether occurred. The reaction mixture was then cooled to room temperature, washed with two 20-ml portions of water, two 20-ml portions of 9% hydrochloric acid, one 20-ml portion of saturated sodium bicarbonate solution, and three 20-ml portions of water, and dried over anhydrous sodium sulfate. Removal of the ether under reduced pressure (water aspirator) gave 6.1 g (92%) of crude *cis*- and *trans*-dibromo esters, which upon recrystallization from 20 ml of *n*-heptane yielded 1.7 g (26%) of *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_t$), mp 86–87°. Further recrystallization from 15 ml of *n*-heptane containing decolorizing charcoal yielded 1.1 g of pure *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_t$), mp 87–88° (lit.[21] mp 87–87.5°).

A mixture of 3.0 g (0.02 mole) of sodium iodide, 15 ml of absolute ethanol, and 2.1 g of the concentrated mother liquor from the above recrystallizations was refluxed for 2 hr. The dark solution formed was cooled and diluted with 20 ml of water and 10 ml of 10% sodium thiosulfate solution. The colorless solution thus obtained was extracted with three 15-ml portions of ether; the combined ether extracts were washed with 5 ml of 10% sodium thiosulfate solution and three 5-ml portions of water and dried over anhydrous magnesium sulfate. The ether solution was concentrated to 15 ml and cooled in a Dry Ice–acetone bath to yield 1.5 g of crude *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_c$), mp 37–40°. One recrystallization of the *cis*-dibromo ester from 2 ml of *n*-heptane gave 1.3 g (20%) of pure *cis*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_c$), mp 40.5–41.5° (lit.[21] mp 41–42°).

**Debromination of *trans*-1,2-Dibromo-1,2-dicarbomethoxycyclobutane (6$_t$).** A 0.6-g (0.0018 mole) sample of *trans*-1,2-dibromo-1,2-dicarbomethoxycyclobutane (**6**$_t$) was debrominated by refluxing for 3.5 hr a solution of the ester in 25 ml of dry ethanol containing 0.9 g (0.006 mole) of sodium iodide. The dark solution was diluted with 30 ml of 3% sodium thiosulfate solution and the resultant clear solution extracted with three 20-ml portions of ether. The combined ether extracts were washed with two 10-ml portions of water and dried over magnesium sulfate. Removal of the ether under reduced pressure afforded 0.31 g of impure 1,2-dicarbomethoxycyclobutene (**7**), mp 41–45°. One recrystallization from *n*-hexane gave 0.16 g (52%) of pure[22] 1,2-dicarbomethoxycyclobutene (**7**), mp 45–46° (lit.[21] mp 45–46°). The nmr spectrum showed two absorption bands, at $\tau$ 7.37 for the six methyl protons and $\tau$ 6.26 for the four ring protons, with an intensity ratio of 3:2.

**Acknowledgments.** We are greatly indebted to Dr. W. B. Moniz (Naval Research Laboratory) for the early 100-MHz spectra, to Dr. R. Freeman (Varian Associates) for reading the manuscript, and to Professor R. M. Moriarty (Catholic University) for helpful comments.

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[19] W. H. Perkin, Jr. *J. Chem. Soc.*, **65**, 572 (1894).

[20] K. B. Alberman and F. B. Kipping, *ibid.*, 779 (1921).

[21] F. B. Kipping and J. J. Wren, *ibid.*, 1733 (1957).

[22] A gas chromatogram of the 1,2-dicarbomethoxycyclobutene, obtained by the use of a TC detector and a 10 ft × 0.25 in. column packed with 20% SE-30 on 30–60 mesh Chromosorb W acid washed with a column temperature of 210° and a flow rate of 100 cc/min, gave only one peak.

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# Charge-Transfer Complexes between Substituted Pyridinyl Radicals

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**Abstract:** The reversible dimerization of 1-alkyl-4-carbomethoxypyridinyl radicals in isopentane solution was studied by measuring electronic absorption spectra at low temperature. Charge-transfer bands associated with the radical dimers were observed for the 1-methyl-, 1-ethyl-, and 1-isopropyl-4-carbomethoxypyridinyl radicals. Analysis of the spectra yields monomer–dimer equilibrium constants at 77°K and molar extinction coefficients of charge-transfer bands of dimers for three radicals. A theoretical study has been undertaken with the pyridinyl monomer and dimer.

Hausser and Murrell[1] reported that the 9-ethylphenazyl radical and the tetramethyl-*p*-phenylenediamine cation radical form dimers in ethanol at low temperature, and that charge-transfer (abbreviated hereafter to CT) bands associated with $\pi$–$\pi$ interaction

[1] K. H. Hausser and J. N. Murrell, *J. Chem. Phys.*, **27**, 500 (1957).