

Figure 1.—(a) Bailar type of transition state; (b) Rây and Dutt transition state.

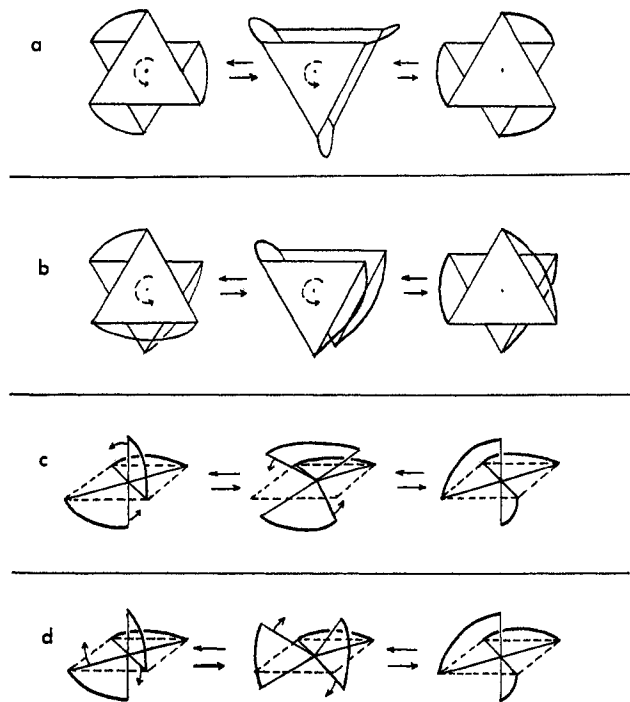


Figure 2.—(a) Bailar twist to produce a Bailar type of transition state; (b) Bailar twist to produce a Rây and Dutt transition state; (c) Rây and Dutt type of twist to produce a Bailar transition state (Springer-Sievers mechanism); (d) Rây and Dutt type of twist to produce a Rây and Dutt transition state.

to either type of transition state depending upon which pair of trigonal faces is chosen for the rotation. The Bailar twist is illustrated by Figure 2a and b.

Springer and Sievers viewed the formation of the two transition states as also being the result of a mechanism which consists of holding one chelate ring stationary while the other two rings swing in opposite directions. As first proposed,² this leads to a Rây and Dutt intermediate. Springer and Sievers pointed out that the same type of motion in the opposite direction would lead to a Bailar transition state. The Springer-Sievers and Rây-Dutt mechanisms, both of which will be referred to generically as Rây and Dutt type of mechanisms, are illustrated by Figure 2c and d.

Springer and Sievers recognized that the Bailar twist and the Rây and Dutt type of twist are really equivalent although their statement to this effect was not put quite so strongly. Their attention was focused primarily on the changes in donor-metal-donor (D-M-D) angles during the rearrangement process and it was never stated explicitly that the Bailar-twist mechanism and the Rây and Dutt type of mechanism are *completely*

identical and that they only appear different because they view the intramolecular twisting process from two different perspectives.

It should be made clear that the differences which appear to exist, from a consideration of the variations in D-M-D angles, are purely artificial. The formation of a Bailar transition state in which the ring D-M-D angles have been compressed may be viewed as the result of a Bailar twist in which the distance between the rotating trigonal faces remains fixed. The motion described by this mechanism is completely equivalent at every point to the motion which occurs during the application of a Rây and Dutt type of twist in which the chelate rings are not rigid and where the ring D-M-D angles decrease. Likewise, the formation of a Bailar transition state in which the ring D-M-D angles are 90° may be looked upon either as resulting from a Bailar twist in which the rotating trigonal faces move apart along the C₃ axis or as the result of the operation of a "rigid-ring" Rây and Dutt type of mechanism. Again, the two mechanisms are identical at each point along the path to the transition state. This exact equivalence holds for any set of D-M-D angles as well as for the formation of a Rây and Dutt transition state.

The apparent general lack of recognition that the differences between the Bailar twist and the Rây and Dutt twist are not real is manifest in at least two places in the very recent literature. Muetterties,⁴ in an analysis of intramolecular rearrangements in six-coordinate species, referred to these two paths as being distinct for tris chelates. In another instance, Broomhead, Dwyer, and Meller⁵ described models to illustrate the Bailar twist and the Rây and Dutt twist. In their article, intended for the teaching of inorganic racemization mechanisms, they failed to make any mention of the complete equivalence of these two paths.

This correspondence does not mean to suggest that one view of the intramolecular twisting mechanism be discarded in favor of another. Indeed, the two perspectives of the nonbond-rupture mechanism complement one another. Rather, it is aimed at correcting what may be an important misunderstanding. It should be absolutely clear that there is basically but one twisting mechanism which can lead to two different types of transition state depending upon its mode of execution.

(4) E. L. Muetterties, *J. Am. Chem. Soc.*, **90**, 5097 (1968).

(5) J. A. Broomhead, M. Dwyer, and A. Meller, *J. Chem. Educ.*, **45**, 716 (1968).

DEPARTMENT OF CHEMISTRY
ST. JOHN'S UNIVERSITY
JAMAICA, NEW YORK 11432

JAMES E. BRADY

RECEIVED NOVEMBER 12, 1968

The 3d Orbitals of Phosphorus and Sulfur¹

Sir:

Since the 3d orbitals of phosphorus and sulfur are not occupied in the normal states of the free atoms,

(1) Supported in part by the Tulane Computer Laboratory, by Esso Research and Engineering Co., and by Freeport Sulphur Co.

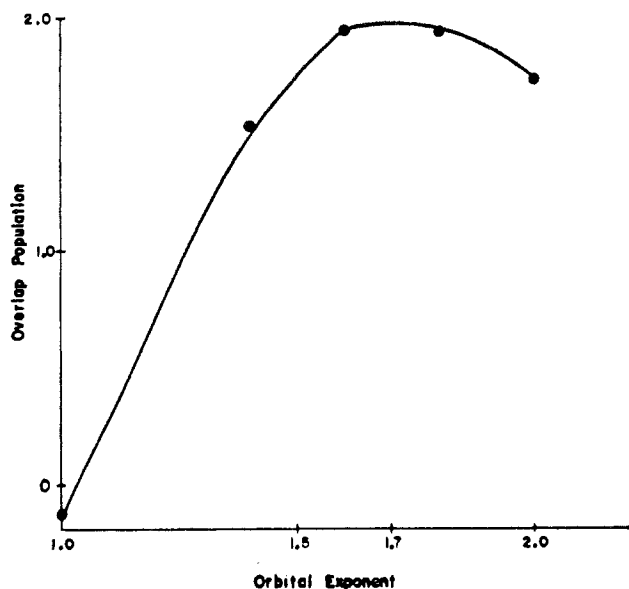


Figure 1.—Nearest neighbor overlap populations as a function of the sulfur 3d orbital exponent in the S_4 molecule. The 3d radial function is proportional to r^2e^{-2r} . In the absence of the 3d orbitals, the overlap population is 1.48.

their explicit functional form must be determined by another criterion. We have examined the values of a number of molecular properties including ionization

potentials, energies of electronic transitions, dipole moments, and overlap populations, computed by a semi-empirical molecular orbital method,² as a function of the 3d orbital exponent z . For the series of phosphorus- or sulfur-containing molecules considered, computed molecular properties are insensitive to the precise value of the orbital exponent over a moderate range centered at 1.4 and 1.7, respectively. The effect of including the 3d orbitals in the basis sets for these molecules is modest, but in the direction of improving agreement between computed and observed properties. These values of z are consistent with the very limited available evidence from *ab initio* calculations.³ Values very much smaller or much greater for the 3d orbital exponents produce pathological results for at least some computed molecular properties. In the absence of more reliable data, these values may be useful for molecular orbital calculations.⁴

(2) L. C. Cusachs and B. B. Cusachs, *J. Phys. Chem.*, **71**, 1060 (1967); L. C. Cusachs and J. R. Linn, Jr., *J. Chem. Phys.*, **46**, 2919 (1967).

(3) D. B. Boyd and W. N. Lipscomb, *ibid.*, **46**, 910 (1967).

(4) NOTE ADDED IN PROOF.—Our predicted value for sulfur is confirmed by F. P. Boer and W. N. Lipscomb, *ibid.*, **50**, 989 (1969).

(5) To whom inquiries should be addressed.

RICHARDSON CHEMICAL LABORATORIES
TULANE UNIVERSITY
NEW ORLEANS, LOUISIANA 70118

W. W. FOGLEMAN
D. J. MILLER
H. B. JONASSEN
L. C. CUSACHS⁵

RECEIVED NOVEMBER 14, 1968