

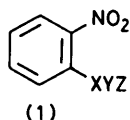
The Isomerisation of Some *ortho*-Substituted Nitrobenzenes: a Structure Correlation Analysis

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A search of the Cambridge Crystal Structure file has revealed a number of benzenoid molecules containing an NO₂ group *ortho* to an XYZ unit. X, Y, and Z are second row atoms, the X atom is bonded to the benzene ring, and the CXYZ unit is essentially planar. A scatter plot of the dihedral angles between the benzene ring and the NO₂ and XYZ groups, respectively, leads *via* the principle of structure correlation analysis to the conclusion that these molecules isomerise by disrotatory torsions of the two substituents, such that the sum of the dihedral angles is always 90°. A degree of resonance stabilisation is thus retained throughout the isomerisation, while non-bonded interactions are minimised. Alternative mechanisms do not satisfy one or other of these conditions.

A CONTINUING area of interest in organic stereochemistry concerns the study of the isomerisation pathways and energetics of molecules comprising a symmetric skeleton substituted by two or more sterically interacting aryl groups. Di-, tri-, and tetra-arylmethanes and cognates, and arylated ethanes, benzenes, cyclopentadienones, and porphyrins all fall within this overall classification.¹ Commonly, variable temperature ¹H and ¹³C n.m.r. techniques have given data which through line-shape analyses have yielded values for isomerisation barriers. Furthermore, it has frequently been possible to deduce an idealised transition state for the isomerisation in question, sometimes with the aid of a permutational analysis of all feasible isomerisations, and thus to infer a mechanism. However, the exact timing of consecutive steps in the isomerisation can never be derived from such experiments. As an alternative, theoretical calculations, usually of the empirical force field (EFF) type, have been applied to appropriate systems and have yielded a more detailed picture of the dynamics of an isomerising molecule.

However, there exist molecules where the rotors are formally analogous to the two-fold aryl groups despite being chemically quite different,[†] but where both the n.m.r. and the EFF methods are difficult to apply, if not totally unsuitable. One such example is the *ortho*-substituted nitrobenzene system of generalised structure (1) where the two rotors are NO₂ and XYZ groups, pivoted about a C-N and a C-X bond, respectively.



Nitroaromatic systems simpler than (1) have been studied by means of EFF calculations,³ despite complications due to differing degrees of resonance stabilisation as the substituents rotate. N.m.r. analysis of (1) would

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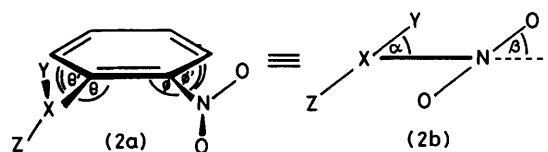
† Recently discussed examples are hexaethylbenzene and its M(CO)₆ complexes, where the ethyl groups can be considered analogous to unsymmetrically substituted phenyl groups, positioned on D_{6h} and C_{3v} skeletons, respectively.²

depend on the presence of suitable magnetic probes in Y and Z, and/or ¹⁷O n.m.r. spectra for the NO₂ group.

In this paper, the dynamic stereochemistry of (1) is discussed from the point of view of a third technique introduced by Bürgi and Dunitz, namely, that of *structure correlation analysis*.⁴ This has been used to deduce mechanistic details of reacting systems, as for instance the nucleophilic addition to carbonyl groups, besides conformational interconversions, as in this paper.⁴

For such an approach to be applicable, it is necessary to have available solid state structural data derived by X-ray diffraction on a series of different but structurally related molecules. Trends in structural variations, if observable, can be equated to the motions which a typical molecule from the series would undergo during a reaction, based on the hypothesis that geometric deformations in the crystal-bound molecule will correspond to the path of least resistance, *i.e.* just such a pathway that a free molecule would follow during a particular interconversion in the absence of crystal packing forces.

Definition of the System.—Resonance stabilisation in (1) is maximal when the NO₂ and XYZ substituents are coplanar with the benzene ring. In this conformation, however, there is an intolerably close approach of one of the NO₂ oxygen atoms to either Y or Z, with the result that one or both groups must rotate out of plane to minimise the unfavourable nonbonded contact. Molecular models, as well as the experimental data to be discussed below, indicate that both substituents undergo torsions about the aryl-X and aryl-N bonds in the same sense, to give a ground state conformation roughly represented by (2a). For convenience, the idealised edge-on projection, (2b), will be used throughout the remainder of this paper. The 'bonds' shown between the atoms of the NO₂ and XYZ groups, respectively, in (2) and subsequent projections are not intended to represent bond multiplicities, but rather atom connectivities only.



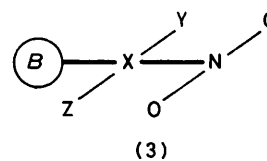
Projection (2b) also shows the dihedral angles, α and β , which define the degree of torsion of the two groups. These are usually measured as the angles between the planes describing the aromatic ring, and the CXYZ unit (α), and the CNO₂ unit (β), respectively.

Other relaxation modes which are less obvious are also to be expected, including changes in the valence angles at the substituted aryl carbon atoms [θ and ϕ in (2a)]. In fact, the two *ortho*-substituents would be expected to move apart such that $\theta > \theta'$ and $\phi > \phi'$ in (2a). Thus, the quantity $\delta = (\theta + \phi) - 240$ can be taken as another, admittedly rough, measure of the repulsive interaction between the NO₂ and XYZ groups.

However, even after relaxation the major nonbonded interactions continue to be between the three NO₂ and the three XYZ atoms, and it is these that will thus usually determine the conformation in the free state. Additional groups attached to Y and Z are assumed to play a relatively minor role in determining the conformation. In the solid state a molecule is exposed to additional weaker intermolecular forces which perturb the ground state geometry to a lesser or greater extent.

For the purposes of the current investigation, the following restrictions have been imposed on the nature of X, Y, and Z. Each is a second row element, and thus approximately the same size throughout the series. Moreover, X and its attached atoms should be essentially

coplanar; most *o*-aminonitrobenzenes are therefore excluded. No species is included where intramolecular hydrogen-bonding is believed to determine the conformation. By means of these restrictions, it is ensured that the XYZ group has steric requirements which are reasonably constant, at least in the all-important region where steric clashing is to be expected. Thus the molecules of the series are consistent with the philosophy of structure correlation analysis; there is sufficient variation in composition to ensure different crystal packing and resultant different conformations in the crystal, but sufficient similarity in steric requirements to be regarded as equally close representatives of the idealised model molecule.



The picture becomes more complicated if (1) is further substituted *ortho* to either XYZ or NO₂. An edge projection is shown as (3), where B is a buttyrressing substituent and could itself be a two-fold rotor (*e.g.* another NO₂ group as in picryl derivatives). A buttyrressing substituent of this type might be expected to play an unwanted

Dihedral and valence angles of nitrobenzenes (4)–(28)

Molecule	Dihedral angles ^a			Valence angles ^{a, b}			Ref.
	α	β	$\alpha + \beta$	θ	ϕ	δ	
Unbuttyrressed species							
(4)	85.6	4.5	90.1	124.7(5)	119.8(5)	4.5	5
(5) ^c	79.5	9.8	89.3	118.8	124.8	3.6	6
(6) ^c	77.4	8.3	85.7	126.0(2)	119.9(2)	5.9	7
(7)	64.7(A)	26.3(B)	91.0	122.7(6)	120.6(6)	3.3	8
(8)	58	28	86	124.2(4)	120.7(4)	4.9	9
(9)	57.1	34.6	91.7	124.6(5)	120.1(5)	4.7	10
(10)	56.2	35.9	92.1	123.1(4)	120.4(4)	3.5	11
(11)	54.0	47.3	101.3	125.4(3.8)	120.4(3.5)	5.9	12
(12)	54	25	79	123(3)	121(2)	4	5
(13)	52.6	40.7	93.3	123.5(8)	120.3(8)	3.8	13
(14)	45.9	46.5	92.4	125.2(3)	119.8(3)	5.0	14
(15)	41.5	46.6	88.1	121.0 ^d	120.3 ^d	0.7	15
(16)	40.2	49.1	89.3	124.2(2)	119.4(2)	3.6	16
(17) ^c	39.4	34.7	74.1	123.4	123.2	6.6	17
(18)	24.1	54.3	78.4	124.6(9)	119.2(9)	3.8	18
(19)	22.2	65.6	87.8	122.6(7)	121.1(7)	3.7	19
(20)	21.6	65.3	86.9	122.3(6)	122.7(6)	5.0	20
(21) ^c	7.0	82.5	89.5	124.9(7)	124.0(6)	8.9	21
Buttyrressed species							
(22)	64(B)	19(A)	83	121	122	3	22
(23)	49	82	131	124	118	2	23
(24)	61	54	115	121.0(2)	118.7(2)	-0.3	24
	61	36	97	123.6(2)	121.0(2)	4.6	
(25)	65	44	109	119.0(3)	120.2(3)	-0.8	25
	65	25	90	124.4(3)	121.6(3)	6.0	
(26) ^c	42.5	49	91.5	124.9	120.1	5.0	26
	42.5	53	95.5	122.6	120.0	2.6	
(27)	61	41	102	116(2)	114(2)	-10	27
(28)	63	32	95	120	125	5	28

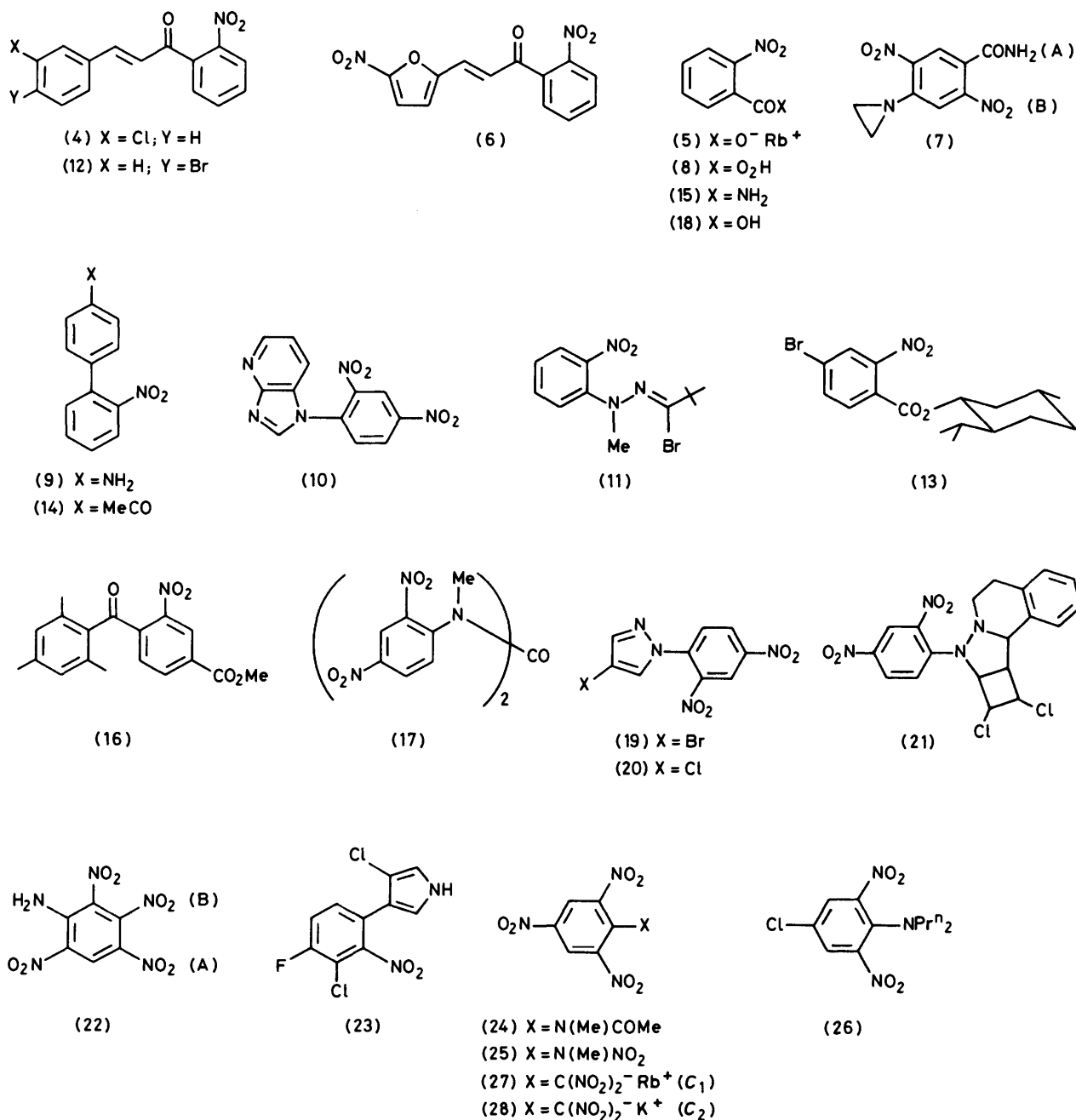
^a See text for definitions. ^b E.s.d.s, where known, are recorded in parentheses. ^c Average of dihedral angles between XY-XZ and adjacent CC bonds, and NO bonds and adjacent CC bonds, respectively. ^d Taken directly from the CSSR print-out. The published values lead to $\delta = -3.9^\circ$.¹⁵

role in determining the conformation of the molecule. However, we have felt justified in including such species in the current discussion for the following reason. In (3), *B* will perturb the conformation of XYZ, but NO₂ is still free to adopt an orientation in sympathy with that adopted by XYZ. Thus, *B* can be viewed as a special case of an external perturbing force on the XYZ-NO₂ system in just the same way that intermolecular forces due to adjacent molecules are assumed to perturb the conformation in the crystal. Clearly those molecules where neither NO₂ nor XYZ is free to relax (doubly buttressed) cannot justifiably be included in the series.

RESULTS

A search of the Cambridge Crystal Data Centre data base *via* the Crystal Structure Search Retrieval (CSSR) system revealed 18 unbuttressed *ortho*-substituted nitrobenzenes (4)–(21) (Scheme) which fall within the classification described above and a further seven buttressed species (22)–(28).^{5–28} Relevant geometric details abstracted from the X-ray structure analyses are recorded in the Table.

The 1,2-disubstituted species are considered first, and since any isomerisation must take place through group torsions, we concentrate on the relationship between the dihedral angles α and β . The over-riding conclusion of this



SCHEME *ortho*-Substituted nitroaromatic compounds of type (1) for which structural data are available

study immediately emerges from the Table, namely, that the sum of α and β is approximately constant at 90° . To emphasise this relationship, a scatter plot of α against β is shown in Figure 1. The straight line derived by least squares correlation of the 18 pairs of values obeys equation (1)

$$\alpha + 1.024\beta = 89.1 \quad (n\ 18; r\ 0.96; s\ 5.9) \quad (1)$$

From the Table, the valence angle distortions, as reflected by δ , are reasonably constant between 3.3 and 8.9° , with the exception of the value for (15) which is anomalously low at 0.7° .

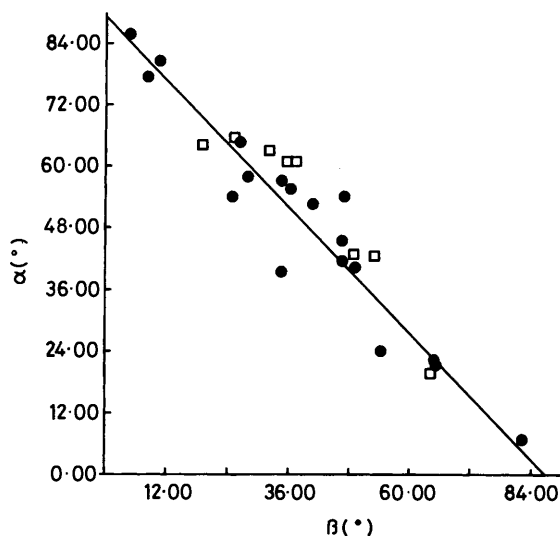
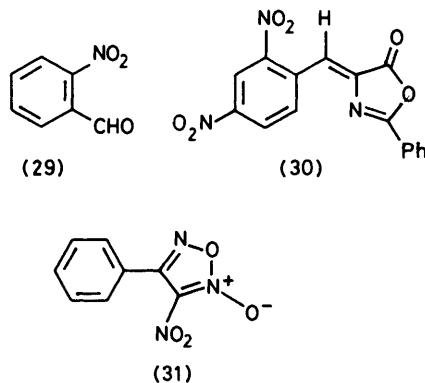


FIGURE 1 Plot of dihedral angle of XYZ (α) versus dihedral angle of NO_2 (β). ●, Unbuttressed species; □, buttressed species. The A/B pair *o*-dinitro-system of (22) is represented by two points

In contrast to molecules (4)–(21), the sums of the dihedral angles, $\alpha + \beta$, of (29) and (30) are only *ca.* 60 and 30° , respectively.^{29,30} In these molecules, the substantially smaller hydrogen atom permits the NO_2 group to remain more nearly coplanar with the benzene ring. Clearly, here, the different overall steric picture precludes the inclusion of (29) and (30) in the series (4)–(21). For a different reason the sum of α and β in (31) is only 64° .³¹ In a system superficially representative of (1), the larger external valence angles of the five-membered ring cause δ to be 20.4° . The non-bonded interactions are correspondingly less because of the greater inherent separation of the groups, and thus the latter need to undergo less torsion despite the NO_2 group being buttressed by an oxygen atom.

Turning attention now to the buttressed series of molecules (22)–(28), the Table reveals that the sum of the dihedral angles, $\alpha + \beta$, is on average higher than in the unbuttressed series. In an attempt to bring the conformational analysis of the buttressed molecules on to the same basis as that of the unbuttressed, a criterion for acceptability of comparison was sought. The quantity δ has been selected for this purpose with the condition that it should be near the same range as for the unbuttressed series. This ensures that whatever additional distorting effects are present due to the third substituent, they leave the steric environment of the two groups of interest, NO_2 and XYZ, relatively constant and comparable with the unbuttressed series.

Inspection of the Table reveals that three NO_2 -XYZ pairs have $\delta < 0$. That is, the NO_2 and XYZ groups are forced by the third, buttressing, substituent toward one another so that they would therefore be expected to have to undergo relatively greater overall torsion to maintain non-bonded contacts within the same acceptable limits. Gratiifyingly, the $\alpha + \beta$ data for these three molecules are in fact



higher than the expected value of 90° . A further anomaly is (23) where the sum of α and β is 131° . The conformation of the NO_2 group is determined by the buttressing *o*-chloro-group (β 82°). A torsional angle of *ca.* 8° would therefore be anticipated for α , in contrast to the experimentally observed value of 49° . However, in a near-planar conformation, the hydrogen atom in the pyrrole 1-position would be particularly unfavourably placed with respect to the *o*- NO_2 group. Here, then, is the first and only breakdown of the assumption that ligands attached to Y and Z are of little consequence in determining the stereochemistry in these systems. The other seven data are considered acceptable within the limitations laid down, and are included in the correlation shown graphically in Figure 1.

DISCUSSION

A relationship has been derived between the angles of torsion of a nitro-group and an *ortho*-substituent in the benzenoid molecules of type (1). How does this relate to the main question of this paper, *viz.*, the isomerisation pathway of such species? According to the principle of structure correlation analysis, the structures of molecules (4)–(28) can be taken as still-frame pictures of a molecule (1) undergoing isomerisation in the free state (*i.e.* not constrained in a crystal lattice). The correlation line of Figure 1 is thus the trajectory of an isomerising molecule in the two-dimensional space defined by the two dihedral angles α and β . Therefore, it can be concluded that (1) isomerises by disrotation of the two rotors, in such a manner that the sum of their dihedral angles is 90° . The overall isomerisation pathway is depicted in Figure 2. Torsion of one of the two groups is not independent of the other; their rotations are said to be *correlated*.³²

To develop the discussion further we begin from the top central conformation in Figure 2, on which one possible direction of group torsions has been arbitrarily

indicated. All the conformations above the line, m , which represents a mirror plane, are chiral. The transition point between one conformation and its enantiomer is idealistically represented by the extreme right conformation straddling m (achiral; C_s symmetry). Further torsion of the two groups leads into the enantiomeric manifold of conformations below m , and thence into the diastereoisomeric manifold, which again eventually enantiomerises *via* an idealised C_s conformation with the nitro-group perpendicular to the aryl plane. The complete isomerisation sequence could occur, of course, with equal likelihood by the reverse pathway.

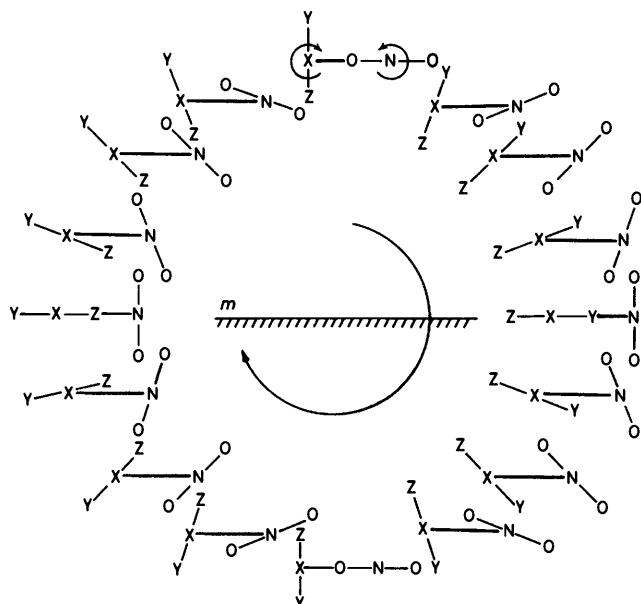


FIGURE 2 Pathway of isomerisation of (1). The arrows on the top central conformation indicate one of the two possible disrotatory motions of the rotors; the clockwise arrow at the centre of the Figure indicates the corresponding sequence of isomerisation steps

It is important to note that although some 1,2,3-trisubstituted systems have been included in the structure correlation, the derived conclusions regarding the dynamic stereochemistry of systems of type (1) in the free state are *not* applicable to these buttressed species. In fact, derivatives (24)–(28) can be considered representatives of C_{2v} skeletons substituted with three interacting rotors. An independent structure correlation for such systems is unfortunately inhibited by a lack of structural data.

The molecules under discussion are representative of an idealised system which has the same point group symmetry (C_2) and dynamic symmetry group ($S_2[S_2] + S_2$) as the broad class of two-bladed propellers, typified by such chemically disparate systems as diarylmethanes and spirocyclic phosphoranes. The permutational analyses of their dynamic stereochemistry are identical,³³ and they are thus said to be *stereochemically correspondent*.³⁴

Besides the lowest energy pathway deduced from the

solid state data, other feasible isomerisation pathways are intuitively possible. These comprise conrotation *via* an idealised planar structure (an enantiomerisation), and conrotation *via* an idealised conformation with both substituents perpendicular to the benzene plane (a diastereoisomerisation) (Figure 3). The former is disfavoured for obvious steric reasons, while the latter presumably entails unnecessary loss of resonance stabilisation at the transition state. In fact, the experimentally deduced mechanism appears to minimise non-bonded interactions while attempting to maximise resonance stabilisation.

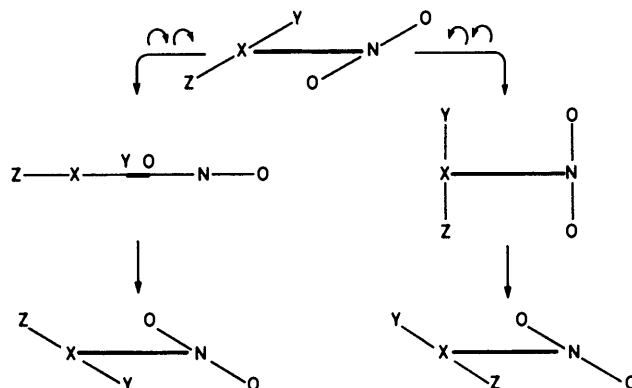


FIGURE 3 Isomerisation of (1) by mechanisms involving conrotation. The Figure shows idealised transition states as well as the overall consequences of the isomerisation

While useful for indicating geometric trends, the whole principle of structure correlation says less about the energetics associated with the process under consideration. Thus it is still not known which of the structures drawn in Figure 2 most accurately represents the transition state of the isomerisation. Judging from the wide spread of α/β combinations observed in the various molecules studied, the barrier to isomerisation is fairly low in (1). Furthermore, from the relative paucity of data corresponding to the conformations with $\alpha 0, \beta 90^\circ$ and to a lesser extent $\alpha 90, \beta 0^\circ$, it might be surmised that these are energetically disfavoured and therefore correspond most closely to the transition state structures. Consistent with this hypothesis are results of extended Hückel calculations³⁵ on an analogue of (19) and (20) which can be interpreted in terms of the disrotatory mechanism deduced in this work. The potential barrier to enantiomerisation *via* correlated rotation was calculated to be $\lesssim 30$ kJ mol⁻¹, with transition state near the conformation $\alpha 0, \beta 90^\circ$, while that for diastereoisomerisation is $\lesssim 5$ kJ mol⁻¹, near $\alpha 90, \beta 0^\circ$. Additional reported barriers to rotation of a nitro-group in nitroaryl systems range from 13 to as high as 59 kJ mol⁻¹.³⁶⁻⁴³ Steric inhibition to torsion would result in yet higher barriers for (1), whereas lower barriers would be expected if the ground state conformation were sterically destabilised. On the basis of the highest value so far reported,⁴³ dynamic n.m.r. delineation of stereochemical exchange processes in (1) is feasible.

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