complex overlapping multiplets centered near τ 10.1 (2 H) and 9.6 (4 H) and a broad singlet at τ 5.40 (2 H). The very high field signals for six protons are just what is expected for **4**. Upon warming the solution to room temperature the signals for **4** disappeared and 1,4-cyclohexadiene (**9**) signals appeared at τ 7.8 and 4.7.

Thermolysis of **4** in pyridine solvent at 25° produced a quantitative yield of nitrogen. Glpc analysis (20% SE-30 on Chromosorb W column) of the reaction solution showed **9** as the only detectable product.[6] Analysis with methylcyclohexane present as an internal standard established that **9** was formed quantitatively (>99%).

The first-order rate constants for decomposition of **4** in pyridine were determined at nine temperatures over the range −5 to +11° by periodic integration of the increasing τ 7.8 protons of **9** against the protons of acetonitrile internal standard. Some kinetic results are given in Table I along with pertinent comparisons to **1**[1] and **2a**.[7]

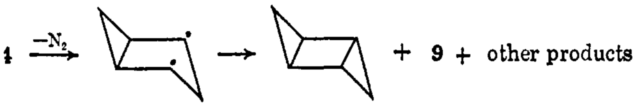
Table I. Thermolysis Rate Data for Some Azo Compounds

Compd	Temp, °C	10^4k, sec^{-1}	Rel rate	E_a, kcal/mole
4[a]	−3.5	0.77[b]	1.6×10^{11}	18.9 ± 1.5[c]
4[a]	+5.5	2.44[b]		
2a	−3.5		1.0[d]	37.3 ± 0.3
1[e]	−3.5		0.01[d]	40.3 ± 0.3

[a] About 0.2 *M* in **4**. [b] Calculated from 25–30 integrations covering the range 0 to *ca*. 80% reaction. [c] Based on an Arrhenius plot of nine rate constants over the temperature range of −5 to +11°. The uncertainty is root-mean-square deviation. [d] Estimation based on gas-phase results and extrapolation to −3.5° from other reported data.[1,7] [e] *cis* isomer.

On the basis of the structural similarity between **4** and system **2**, a possible mechanistic process for the thermolysis of **4** is outlined in Scheme II.[2] If **4** reacts *via* a 1,3-diradical intermediate(s) one expects at least some ring closure with a great propensity for inversion of configuration to give *trans*-tricyclo[3.1.0.0^{2,4}]hexane (**10**).[2,8] On the contrary, 1,4-cyclohexadiene (**9**) is the only product observed. Our analytical method would have detected the presence of <0.1% **10**.[4,6] Control experiments showed that **10** and the other C_6H_8 hydrocarbons are completely stable under the thermolysis conditions. The extremely high product specificity from **4** strongly suggests that **4** and **2** decompose by different mechanisms.

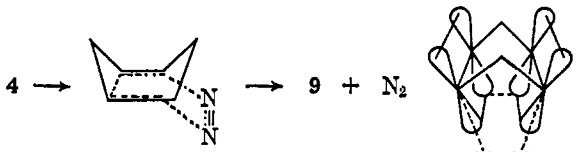
Scheme II



The exceptionally high reactivity of **4** also is not consistent with the decomposition of **4** by Scheme II. A reactivity ratio of 10^{11} is many orders of magnitude greater than it should be if **4** and **2** decompose by similar mechanisms. For instance, the reactivity ratio for **2a**, **2b**, and **2c** is only 1.0:6.0:0.9.[2]

A more plausible mechanism which accounts for the results involves synchronous nitrogen elimination and 1,4-cyclohexadiene (**9**) formation as illustrated by Scheme III. Such a concerted route is an orbital-symmetry-allowed process.[9] The cyclopropane bonding orbitals in **4** are especially favorably oriented for overlap with the developing orbitals at C_1 and C_5 in the transition state for nitrogen departure (see end-view **11**). In this regard, Berson and Olin[10] have reported an interesting stereochemical study of the thermolysis of the 3,4-diazabicyclo[4.1.0]heptyl system which shows a strong preference for a transition state of similar geometry. It is noteworthy that the spatial orientation of the cyclopropyl ring in **4** is comparable to the favored relationship found in other kinds of reactions which show marked rate enhancement due to cyclopropyl participation.[11,12]

Scheme III



In addition to the electronic factor, relief of steric interaction between C_8 and C_8 hydrogen atoms and the additional strain imposed by the cyclopropyl ring undoubtedly make some contribution to the enormous 10^{11} rate acceleration found with **4**. At present there is not sufficient information for making a separation of the three effects. We have experiments under way which are aimed at estimating how much is due to each factor.

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(6) With our analytical conditions all C_6H_8 hydrocarbons such as tricyclo[3.1.0.0^{2,4}]hexane (**10**),[4] bicyclo[3.1.0]hexene, 1,3-cyclohexadiene, etc., were readily detectable.

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A Pure Intramolecular Charge-Transfer Transition. Substituted N-Alkyl-N-nitrosoanilines[1]

Sir:

While intramolecular charge-transfer bands in absorption spectra have been postulated for some time,[2]

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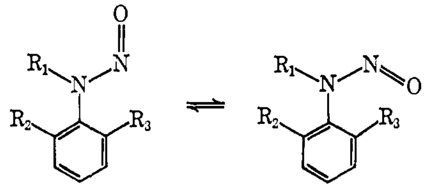
(2) J. N. Murrell, *Quart. Rev.* (London), **15**, 191 (1961).

Table I. Resolved Spectra of Twisted N-Nitrosoanilines in Cyclohexane[a]

Compd	R_1	R_2	R_3	*syn*:*anti*	^1L_b λ_{max}, nm ($\epsilon \times 10^{-3}$)	$^1B_{NNO}$ λ_{max}, nm ($\epsilon \times 10^{-3}$)	$^1CT^c$ λ_{max}, nm ($\epsilon \times 10^{-3}$)	^1L_a λ_{max}, nm ($\epsilon \times 10^{-3}$)
1	*i*-C_3H_7	H	H	65:35		255 (5.3)	226 (3.3)	209 (9.5)
2	*t*-C_4H_9	H	H	1:99	276^b (0.42)	251^b (3.7)	228 (4.6)	209 (7.3)
3	CH_3	CH_3	H	83:27		251 (6.1)		212 (11)
4	*i*-C_3H_7	CH_3	H	36:64	274^b	244^b (5.2)	228^b (1.2)	211 (11)
5	CH_3	CH_3	CH_3	78:22	275^b (0.33)	239^b (6.2)		212 (11)
6	*i*-C_3H_7	CH_3	CH_3	29:71	275^b (0.26)	242^b (5.0)		213 (12)

[a] The compounds are listed in the order of estimated increasing twist. [b] These bands appear as shoulders in the raw spectra; the tabulated λ and ε values were taken from the Du Pont curve resolver results. [c] Intensities are calculated on the basis of total concentration of both isomers.

the actual charge-transfer character of many such bands has recently been questioned.[3] We have now found a band which can unequivocally be assigned as an intramolecular charge-transfer band in the electronic spectra of certain twisted nitrosoanilines (I ⇄ II), *i.e.*, a transition which involves the transfer of more than half an electron from the NNO group to the benzene ring.



I (*syn*) II (*anti*)

R_1 = Me, *i*-Pr, *t*-Bu; R_2 = H, CH_3; R_3 = H, CH_3

Nitrosoanilines exist in two isomeric forms, *syn* (I) and *anti* (II), which are in thermodynamic equilibrium at room temperature; their ratios may be determined from integrations of their nmr spectra.[4] It has been suggested[4] that N-isopropyl-N-nitrosoaniline (**1**) is twisted about the aromatic C–N bond, since its absorption spectrum shows a 25-nm hypsochromic shift of the longest wavelength π–π* band, relative to that of N-methyl-N-nitrosoaniline.

We have prepared a series of nitrosoanilines which are severely twisted, to varying degrees (θ), by substitution of one or two methyl groups in the 2 and 6 positions of the ring. The isomer populations were determined by nmr; the electronic spectra were obtained in cyclohexane and ethanol, and all bands were resolved into Gaussian functions using a 310 Du Pont curve resolver.[5] The spectral results in the 200–300-nm region are reported in Table I, along with the band assignments.

The spectra of the most highly twisted nitrosoanilines (**5** and **6**, where θ is assumed to approximate 90°) may be explained as a sum of the absorption bands of two chromophores, each independent of the other. Bands arising from the benzene chromophore appear near 275 nm (^1L_b) and 212 nm (^1L_a), and are quite similar, in both position and intensity, to those expected for alkyl-substituted benzenes. The $^1B_{NNO}$ band arises from a localized π–π* transition of the NNO chromophore; it appears near 240 nm and is similar to the ^1B band observed in dimethylnitrosamine (λ_{max} 232 nm (ϵ 5.9×10^3)).

As θ is decreased to something less than 90° (as in **1**, **2**, and **4**), the $^1B_{NNO}$ band shifts bathochromically because of the increased interaction with the benzene ring and tends to obscure the ^1L_b band; the ^1L_a band is shifted slightly to the blue because of the decreased substitution on the benzene ring. But in these compounds, an additional band of varying intensity appears near 228 nm. This band is extremely sensitive to solvent effects, showing both hypso- and hypochromic shifts in ethanol.

Using CNDO-CI calculations,[6] theoretical predictions of the electronic absorption spectra have been obtained for both *syn* and *anti* isomers of these compounds in varying degrees of twist about the C–N bond. For the twisted (θ = 90°) *anti* isomer, these calculations predict a transition having as its major CI component a charge-transfer spin configuration. This configuration arises from the promotion of an electron in an MO perpendicular to the π system on the NNO group to a purely benzene antibonding MO. The remaining CI components of this band are localized benzene transitions. A similar transition is calculated for the *syn* isomer at somewhat higher energy.

We assign this theoretically predicted transition in the *anti* isomer to the observed band at 228 nm and propose that it has predominantly charge-transfer character. This assignment is consistent with the observation that the intensity vanishes in the completely twisted compounds (θ near 90°). In these compounds, the MO from which the electron is being excited has purely (or almost purely) lone-pair character on the NNO group, and the orbital to which this electron is excited is a localized benzene orbital. Consequently, no one-center components occur in the intensity integral, and the intensity is very low. As soon as the twist is somewhat relieved, the two orbitals involved become more delocalized, one-center terms occur in the integral, and the intensity becomes significant. The apparent observation that the band is not observed in the *syn* isomers is ascribed to the higher energy of the ^1CT band in these compounds, which probably places them under the more intense ^1L_a band. The hypsochromic and hypochromic shifts observed upon addition of a protic solvent (EtOH) confirm this assignment, since they are characteristic of transitions involving "nonbonding" orbitals.

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(5) We thank the Procter and Gamble Co. and Dr. W. Yellin for the use of the Du Pont curve resolver.

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