Crystal Structure of 1,2-Diphenyl-3-nitrocyclopropene and ab Initio Calculations of 3-Nitrocyclopropene

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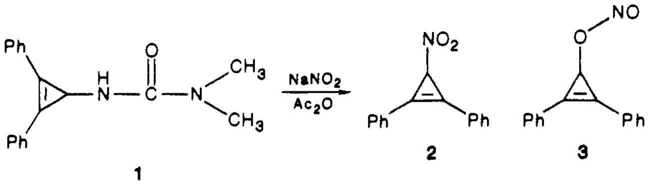
Abstract: The structural ambiguity regarding the identity of the reaction product of 1,2-diphenylcyclopropenium perchlorate and sodium nitrite in acetic anhydride has been resolved in favor of the 3-nitrocyclopropene alternative. The molecule in the solid state adopts the bisected conformation, compatible with the theoretically calculated structure and characteristic of other π-acceptors attached to three-membered carbocyclic rings. The ring dimensions and especially the very long C–N bond indicate a tendency toward unprecedented facile heterolysis of the C–NO_2 bond to form nitrite anion and a cation; this tendency is only slightly apparent in the isolated (model) 3-nitrocyclopropene.

In a search for potential diazocyclopropene precursors, Jones and Kobzina[1] attempted the nitrosation of *N′*,*N′*-dimethyl-*N*-(2,3-diphenylcyclopropenyl)urea (**1**). The product was a colorless crystalline substance whose structure was formulated as either the nitro derivative **2** or the nitrite ester **3**. Although much of the spectral evidence clearly favored the nitro structure **2**, the conditions of formation (S_N1), the ease of ionization, and certain features of the mass spectrum provided some support for the nitrite ester structure **3**.



The detonation of a sample of diphenylcyclopropenium perchlorate (an alternative source of **2**) in the hands (literally) of one of us and the very poor diffracting properties of superficially very beautiful crystals of the title compound obtained from acetonitrile solution delayed the resolution of this structural question for some time. Eventually, suitable crystals of this substance were obtained from nitromethane solution, and the crystal structure was determined. The results, which confirm the IR, NMR, and UV spectral data supporting the nitro formulation **2**, are depicted in Figure 1. (See Tables I and II for structural details.)

Although there are a few reports of crystal structures containing a nitro group attached to a cyclopropane,[2-4] to our knowledge this constitutes the first report of a nitrocyclopropene, and the molecular geometry of this structure exhibits some interesting features. The observed bisected conformation of the nitro group with respect to the ring is wholly expected on the basis of the observed bisected conformations of nitrocyclopropanes and the conformational similarity between other cyclopropanes and related cyclopropenes with π-acceptor substituents.[5-8] (In the bisected conformation, the plane of the substituent's N and two O atoms bisects the cyclopropane ring; in the perpendicular conformation the group is rotated 90°.) This well-known preference of π-acceptor groups for the bisected conformation follows from the interaction of the highest occupied Walsh-type (3e) orbital on the cyclopropane[9] with the lowest unoccupied (π*) orbital of the acceptor group. Since cyclopropene possesses the same relevant orbitals as cyclopropane,[10] the bisected conformation is expected for similar reasons.

Table I. Atomic Coordinates (Å × 10^4) of 1,2-Diphenyl-3-nitrocyclopropene (**2**)

atom	*x*	*y*	*z*
C(1)	710 (5)	55 (2)	1112 (2)
C(2)	2394 (5)	392 (2)	1500 (2)
C(3)	1955 (5)	1031 (2)	787 (2)
C(4)	3931 (5)	294 (2)	2117 (2)
C(5)	5828 (5)	951 (2)	2193 (2)
C(6)	7339 (6)	811 (3)	2692 (2)
C(7)	6991 (7)	30 (3)	3272 (2)
C(8)	5079 (7)	−606 (3)	3276 (2)
C(9)	3573 (6)	−486 (3)	2708 (2)
C(10)	−1099 (5)	−701 (2)	962 (1)
C(11)	−2534 (6)	−476 (2)	373 (2)
C(12)	−4252 (6)	−1193 (3)	245 (2)
C(13)	−4575 (7)	−2148 (3)	695 (2)
C(14)	−3166 (7)	−2371 (3)	1279 (2)
C(15)	−1445 (6)	−1665 (2)	1420 (2)
N	976 (5)	2228 (2)	864 (2)
O(1)	−59 (5)	2476 (2)	1424 (2)
O(2)	1301 (5)	2884 (2)	333 (1)

The exocyclic bonds to the phenyl substituents, C(1)–C(10) (1.441 (6) Å) and C(2)–C(4) (1.442 (6) Å), are virtually identical with the comparable bonds in 1-phenyl-2-methylcyclopropenecarboxylic acid (1.448 Å)[11] and the corresponding 3,3-bis(methoxycarbonyl) analogue (1.446 Å).[12] The phenyl rings C(4)–C(9) and C(10)–C(15) are nearly parallel to the cyclopropene ring, with angles between their least-squares planes of −8.0 and +8.5°, respectively. The endocyclic cyclopropene double bonds in the carboxylic acid and dimethyl ester above appear

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[𝒮] To whom inquiries regarding the theoretical calculations should be addressed.

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Table II. Calculated (3-21G) Energy and Structural Parameters[a]

Part a[b]

	D-3-NCP (expt)	3-NCP (bisected)		3-NCP (perpendicular)		2-NP (3-21G)	NCPA (3-21G)	
		STO-3G	3-21G	STO-3G	3-21G		bisected	perpendicular
total energy, au		315.116 98	317.459 57	315.110 95	317.449 97	319.906 49	318.694 91	318.683 46
rel energy, kcal/mol		0	0	+3.8	+6.0		0	+7.2
C(1)–C(2), Å	1.300	1.281	1.282	1.285	1.290		1.508	1.492
C(2)–C(3), Å	1.483 (av)	1.480	1.489	1.479	1.481	1.536	1.502	1.521
C(3)–N, Å	1.523	1.537	1.487	1.543	1.492	1.495	1.454	1.472

Part b[c]

	3-NCP (bisected)		3-NCP (perpendicular)	
	6-31G	6-31G*/6-31G	6-31G	6-31G*/6-31G
total energy, au	319.129 79	319.303 95	319.121 91	319.296 02
rel energy, kcal/mol	0	0	+4.9	+5.0
C(1)–C(2), Å	1.490		1.482	
C(3)–N, Å	1.482		1.490	

[a] Additional comparisons are afforded by 3-21G data for 3-methylcyclopropene ($E_T = -153.984\,21$ au; C(1)–C(2), 1.284 Å; C(1)–C(3), 1.520 Å; C(3)–C(4), 1.520 (Å); bisected 3-cyclopropenecarboxaldehyde ($E_T = -227.252\,69$ au; C(1)–C(2), 1.274 Å; C(1)–C(3), 1.528 Å; C(3)–C(4), 1.481 Å); perpendicular 3-cyclopropenecarboxaldehyde ($E_T = -227.241\,38$ au, rel. B = +7.1 kcal/mol: C(1)–C(2), 1.284 Å; C(1)–C(3), 1.518 Å; C-(3)–C(4), 1.498 Å). [b] The bisected and perpendicular conformers of 3-nitrocyclopropene (3-NCP), 2-nitropropane (2-NP), and the bisected conformer of nitrocyclopropane (NCPA) as well as selected experimental (X-ray) structural parameters for 1,2-diphenyl-3-nitrocyclopropene (D-3-N-CP). Obviously C(1)–C(2) for nitrocyclopropenes refers to distal bonds, while C(2)–C(3) in nitrocyclopropane refers to the distal bond. [c] 6-31G optimized and 6-31G*/6-31G calculated energies and structures for the conformers of 3-NCP.

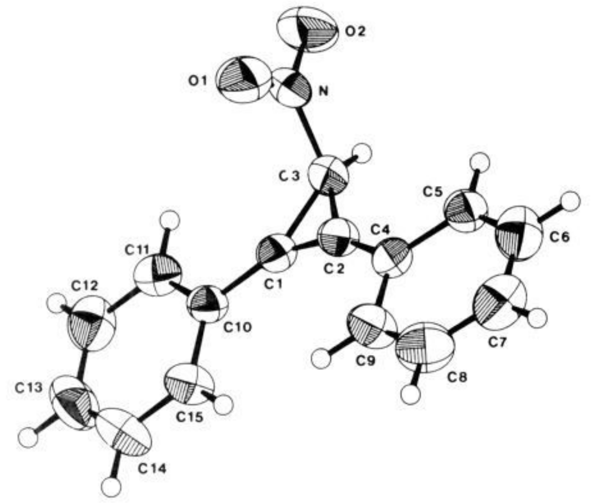

Figure 1. ORTEP diagram for 3-nitro-1,2-diphenylcyclopropene. (See Tables I and II for structural parameters.)

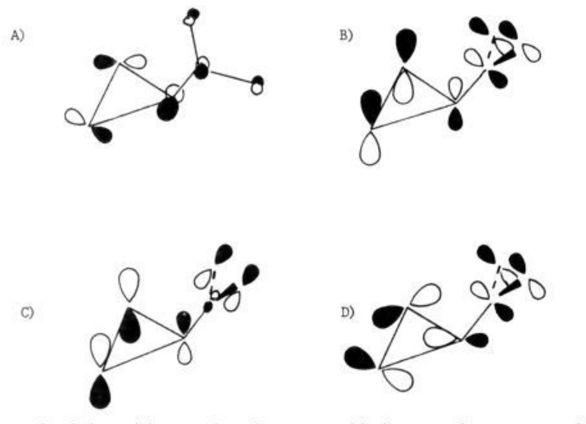

Figure 2. Selected interactions between orbitals on cyclopropene and those on a nitro substituent at the 3-position: (A) interaction between Walsh-type orbital and NO_2 π-LUMO; (B) interaction between cyclopropene π-HOMO and nitro π-LUMO in perpendicular conformer; (C) interaction between cyclopropene π-HOMO and NO_2 n_0 HOMO in perpendicular conformer; (D) interaction between Walsh-type orbital and NO_2 π-LUMO in perpendicular conformer.

somewhat shortened (1.275 and 1.283 Å, respectively) compared with the title compound (1.300 (6) Å) and other cyclopropenes without π-acceptor substituents. The general characteristic effect of π-acceptor substituents at C(1) on the internal bonds of cyclopropanes, is to shorten the distal (C(2)–C(3)) bond and lengthen the vicinal (C(1)–C(2), C(1)–C(3) bonds. Furthermore, the extent of bond length distortion is quantitatively related to the conformation of the substituent group, with the maximum effect occurring at the bisecting position, where interacting π-overlap is greatest. While there are really insufficient data to attempt a similar quantitative correlation in the case of cyclopropenes containing π-acceptor groups, the values for the C=C double-bond length (1.275–1.286 Å) in examples reported to date[5] are suggestive of a comparable trend. The title compound may then, in fact, be anomalous in that the NO_2 group is a very powerful π-acceptor, and yet the cyclopropene double bond does not appear significantly shortened. It is unlikely that the lack of expected shortening is the result of a compensating effect by the second phenyl group attached to the cyclopropene ring.

What is perhaps more interesting is the apparent bond shortening of the vicinal bonds: C(1)–C(3) (1.483 (6) Å) and C-(2)–C(3) (1.482(6) Å)[13] are significantly shorter than typical bonds in cyclopropenes with π-acceptor substituents,[5,7,8] which fall in the range 1.500–1.544 Å (average 1.521 Å). In addition, the C(3)–N length of 1.523 (6) Å is significantly longer than the 1.476–1.486-Å range exhibited by nitrocyclopropanes,[2-4] which are in accord with the 1.488-Å C–N distance of nitrocyclopropane itself from microwave spectral data.[15]

What this interesting pattern appears at first to suggest is that, in the solid state, the C–N bond of the title compound has some ionic character. This partial ionic character is supported by both the mass spectrum and the relative ease of ionization of this substance in solution.[1]

Since this report represents the first example of a nitrocyclopropene, and since the observed C–N bond lengthening suggested a degree of ionic character, we sought to obtain further insight into the nature of this molecule by carrying out ab initio molecular orbital calculations on the parent compound.

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(13) The application of rigid-body libration analysis correction raises these values to 1.488 and 1.487 Å, respectively, but since values from other crystal structures used for comparison are uncorrected, the use of uncorrected values here provide for a more meaningful comprison.

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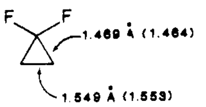
Experimental Section

The title compound was prepared according to the procedure described by Jones and Kobzina.[1] *1,2-Diphenylcyclopropenium perchlorate is sometimes explosive to touch and must be treated extremely cautiously!* Crystals suitable for diffraction were obtained by slow evaporation of a nitromethane solution. Lattice parameters a = 6.147 (2), b = 11.630 (3), c = 17.569 (4) Å, and $\alpha = \beta = \gamma = 90.0°$ were determined by least-squares fit of 25 carefully centered reflections between 20 and 25° of 2θ. An approximate density measurement of 1.3 g cm^{-1} indicated that 4 molecules of composition $C_{15}H_{11}NO_2$ occupied the unit cell with volume 1256.0 (4) Å^3 and calculated density 1.256 g cm^{-1}. The space group determined from systematic absences was $P2_12_12_1$. All unique data with $3.5° < 2\theta < 50°$ and *hkl* maxima of 7, 13, and 19, respectively, were collected with a Nicolet R3M/E autodiffractometer using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and variable-speed (4.88–29.30° min^{-1}) 2θ scans, with three standard reflections (004, 020, 040) measured every 97 reflections. Of the 1337 unique reflections, 19 were rejected and 1080 had $F_o > 2.5\sigma(F_o)$ and were considered observed. The intensities were corrected for Lorentz and polarization effects, a profile analysis correction was applied, but no correction for absorption was made. The structure was solved and refined with the SHELXTL[16] series of programs. Blocked-cascade least-squares refinement with anisotropic non-hydrogen and riding hydrogen atoms with C–H distances fixed at 0.96 Å and isotropic temperature factors fixed at 1.2× the U_{eq} of the bonded carbon atoms converged to a conventional crystallographic residual of 0.046 and weighted residual of 0.053, for all observed reflections. A list of atomic coordinates is given in table I.

Calculated Structure of 3-Nitrocyclopropene

The crystallographic results cited earlier raise some interesting issues. First, are the solid-state ring dimensions really indicative of the isolated molecule structure; i.e., could the seeming anomaly of weak conjugation, evidenced by the observed ring dimensions and a long C–N bond, with the strong π-withdrawing NO_2 be a function of the solid state? Second, what is the intrinsic energy difference between bisected and perpendicular conformers, and what are the isolated molecular dimensions of each? Third, what is the extent and significance of long-range interactions between the double bond and the nitro group in the perpendicular conformer? In order to investigate these issues we have undertaken an ab initio molecular orbital calculational study of 3-nitrocyclopropene using the GAUSSIAN 82 program series.[17] Most of this study has employed the 3-21G basis set,[17] which provides excellent agreement with gas-phase electron diffraction data for 1,1-difluorocyclopropane (**4**)[18] and microwave data for cyanocyclopropane (**5**).[19a,b] The experimental data for **4** and **5** are listed in parentheses. In addition, some calculations are performed using the 6-31G and 6-31G* basis sets in order to verify the 3-21G conclusions.



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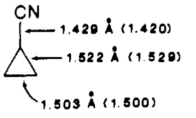

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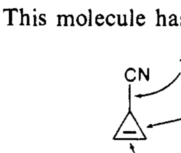
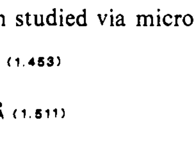
Table IIa lists calculated optimized structures and energies for 3-nitrocyclopropene in both bisected and perpendicular conformations at the STO-3G and 3-21G levels. For the sake of comparison, the experimental values for 1,2-diphenyl-3-nitrocyclopropene are included as are the 3-21G calculated data for nitrocyclopropane and 2-nitropropane. Both the STO-3G and 3-21G basis sets indicate that the bisected conformer is more stable, with the split basis set predicting the larger energy difference. The ring conjugation in the bisected conformer is apparent from the shortening of the distal (C=C) bond by 0.008 Å, the lengthening of the vicinal bonds by 0.008 Å, and the shortening of the C–N bond by 0.005 Å in the bisected relative to the perpendicular conformer (the C–N bond is also shorter than that of 2-nitropropane by 0.008 Å). The C–N bond in the bisected conformer of nitrocyclopropane is very short (1.454 Å), but in good agreement with observed X-ray values (1.451 and 1.469 Å) for *trans*-1,2-dinitrocyclopropane, which were in good qualitative agreement with 4-31G calculations (1.450 Å).[20] However, the calculated distal bond is still much shorter than the corresponding experimental value in 1,2-diphenyl-3-nitrocyclopropene. Even more striking is the experimental C–N bond length, which is 0.036 Å longer than the 3-21G calculated value. In order to see whether this discrepancy might disappear with a larger basis set, full optimization was done at the 6-31G level, and the data are displayed in Table IIb. While the ring bonds lengthen somewhat relative to the 3-21G predictions, the C–N bond is shorter yet. Calculation at the 6-31G* level using the 6-31G optimized structures indicated that the bisected conformer is 5.0 kcal/mol more stable than the perpendicular conformer. Although the possibility exists that configuration interaction and electron correlation could change this geometry, we have chosen to avoid the expense involved in calculations using such approximations for full optimization of 3-nitrocyclopropene. (A reviewer has pointed out that 3-21G bond lengths are generally shorter than MP2/6-31G* optimized values and that this might account for part of the reported effect. While this may be true, comparison of the 3-21G calculational and experimental data in Table I indicates that the disparity between X-ray bond lengths, especially C–N in **2**, is beyond the errors introduced by use of the 3-21G basis set.) Instead, we feel that the experimentally observed tendency toward a shorter than calculated vicinal bond, a longer distal bond, and especially, the long C–N bond indicates a tendency toward ionization betrayed in the solid state. There are no unusual intermolecular contacts for **2** (see Figure 3)—there is an intermolecular contact between O(2) and the H attached to C(3) of a translated molecule. But the distance (2.708 Å) does not appear to be particularly short. The favoring of a zwitterionic structure in the solid state relative to the gas phase certainly has precedent in the comparison between the N–Si bond length in crystalline 1-methylsilatrane (**6a**) (2.175 Å) versus the value in the gas phase (**6b**, 2.45 Å).[21]

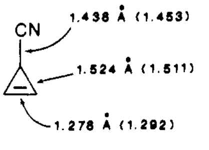


6a (solid state)



6b (gas state)

We close this section by noting that the C–CN bond in 3-cyanocyclopropene (**7**) is calculated to be 0.009 Å longer than that in cyanocyclopropane while, surprisingly, the vicinal bonds are longer and the distal bond is shorter than in 3-nitrocyclopropene. This molecule has been studied via microwave and



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calculations by Staley et al.[22] Our conclusions are consistent with their findings. Clearly, the ring NO_2 and ring CN bonds are

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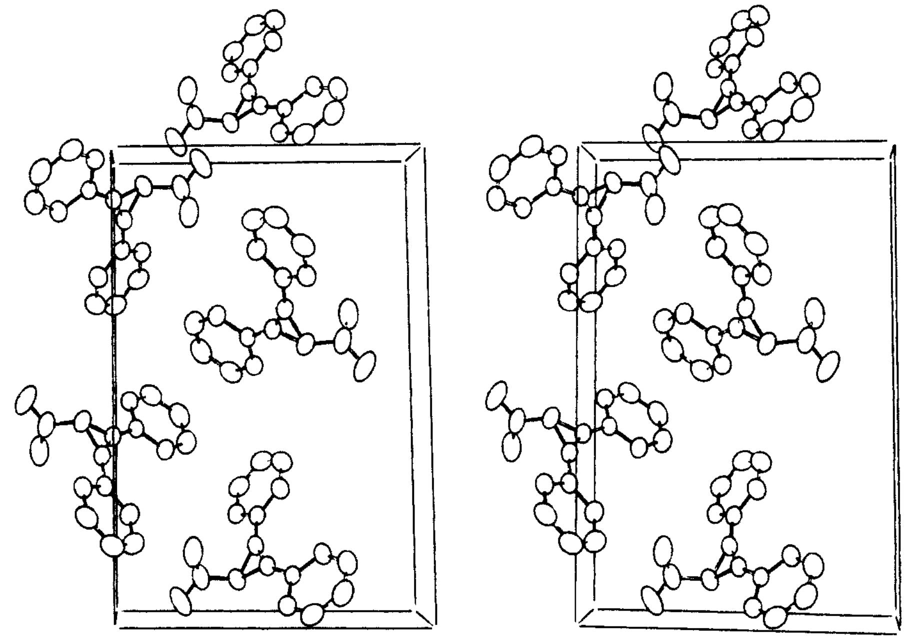


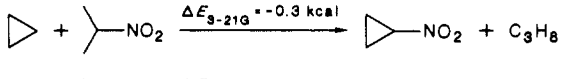
Figure 3. Stereoplot of unit cell contents.

longer in the 3-substituted cyclopropenes than in the cyclopropanes. However, the crystallographic result indicates a lengthening much greater than the calculation predicts. While the longer ring substituent bond in the 3-substituted cyclopropenes relative to the analogous cyclopropanes may indicate slight dipolar character in the cyclopropenes,[22] the result is clearly enhanced in the solid state and possibly further helped by the attached phenyl substituents, although our earlier discussion indicated no apparent structural effects.

The long C–NO_2 bond is certainly consistent with the ease of ionization found experimentally for this molecule.[1] It appears to represent the first documented case of facile heterolysis of a C–NO_2 bond to form a nitrite ion and a carbocation. (Heterolysis of the C–NO_2 group to yield nitrite ion and a radical is a known reaction[23].) The reversible formation of the nitro derivative rather than the nitrite is consistent with the experimental and high-level calculational data, which indicate that nitromethane is more stable than methyl nitrite.[24] (An even greater enthalpy difference has also been reported[25].)

Energetics of Substitution in 3-Nitrocyclopropene

The energetics (3-21G) of substitution of the nitro group on cyclopropane and cyclopropene (bisected conformers in each case) are compared in homodesmotic eq 1 and 2.[26] Here it is seen that



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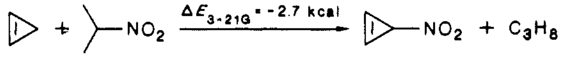
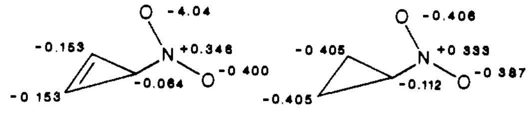
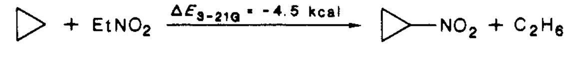


(2)

slightly greater stabilization occurs in 3-nitrocyclopropene, and this is probably consistent with the inherent transfer of negative charge from the double bond to C(3) in the parent hydrocarbon,[27] now stabilized by the electronegative substituent. The same effect is seen in isodesmic reactions 3 and 4. Comparison with eq 5 and 6 shows that the effects of cyano substitution are similar but smaller in magnitude.

Chart I





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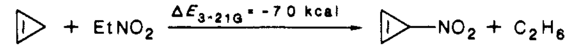

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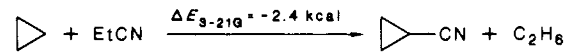

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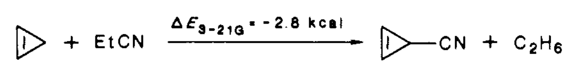

(6)

The ability of the π-bond in cyclopropene to engage in long-range interactions with suitable groups attached at C(3) is exemplified by the strong conjugation between distant double bonds in 3,3′-dicyclopropenyl.[28] In the bisected conformation, interaction between a Walsh-type cyclopropane-like HOMO and the substituent π-LUMO (Figure 2A) will, of course, produce the structural changes predicted by Hoffmann and discussed above. It is less clear what the dominant orbital interactions will be in the perpendicular conformation. Interaction between the cyclopropene π-HOMO and the substituent π-LUMO is one possibility (Figure 2B). Other possibilities include four-electron interaction between the cyclopropene π-HOMO and an occupied nonbonding orbital on the substituent (Figure 2C) or the cyclopropene Walsh orbital/LUMO interaction depicted in Figure 2D.

The 3-21G basis set predicts that the HOMO of the bisected conformation of 3-nitrocyclopropene (ψ_{22} –0.417 au) is of the type n with ψ_{21} (–0.422 au) having some C=C character; the highest Walsh-type orbital is ψ_{18} (–0.483 au). In contrast, the HOMO for the perpendicular conformation (ψ_{22} –0.411 au) has some C=C character, while ψ_{21} (–0.414 au) is an n_0 orbital and the highest Walsh orbital is ψ_{20} (–0.460 au).

Charges on the atoms (3-21G) depicted in Chart I show no special charge separations in 3-nitrocyclopropene when compared with nitrocyclopropane. This again is consistent with essentially normal C–N bonding in the isolated molecules.

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Conclusions

The following conclusions may be derived from this study:

(1) X-ray crystallographic work indicates that 1,2-diphenyl-3-nitrocyclopropene exists as the bisected conformer in the solid state. Ab initio calculations on 3-nitrocyclopropene indicate that this is true for the gas phase as well.

(2) The ring bond lengths (long C(1)-C(2), short C(1)-C(3)) and especially the long C-N bond length are anomalous for a strong π-acceptor such as NO_2 attached to the ring. Part of this is due to a natural tendency toward longer C substituent bonds at C(3) relative to cyclopropane, perhaps due to a "trace" of cyclopropenium character.[22] These effects are seen in the calculational results that represent gas-phase molecules. Most striking is the very large lengthening of the C-N bond in the solid state, which seems to indicate considerable zwitterionic character. There is precedent for favoring a zwitterionic structure in the crystalline state. Additionally, examination of the 3-21G optimized structure of 1,2-dimethyl-3-nitrocyclopropene indicated no significant structural change relative to 3-nitrocyclopropene. The methyl groups should mimic phenyl substituents, which should also stabilize a zwitterion by stabilizing cyclopropenium cation. The calculated result indicates very little zwitterionic character for the dimethyl and probably the diphenyl derivatives in the gas phase.

(3) The results indicate, along with the previously reported experiments of Jones and Kobzina,[1] that the title compound readily ionizes to nitrite and a carbocation, representing the first documented case for a C-NO_2 compound. The long C-NO_2 bond in the crystalline state exemplifies the Bürgi-Dunitz concept of predicting molecular dynamics from statics.[29,30] Thus, in principle, the X-ray structure could have been a predictor for the observed ionization.

(4) Electronegative substituents appear to be more stable thermodynamically at C(3) in cyclopropene than at a cyclopropane carbon.

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Supplementary Material Available: Listings of bond lengths and angles (Table S1), torsion angles (Table S2), and anisotropic temperature factors (Table S3) (3 pages); observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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An Experimental and Computational Study of the Formation of (π-Allyl)palladium Complexes from Olefins and Palladium(II) Salts

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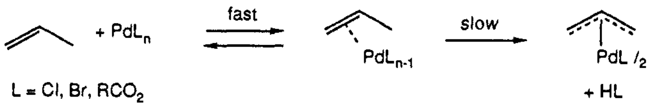
Abstract: Three general mechanisms are considered for the conversion of methylenecyclohexene by Pd(II) salts to the corresponding (π-allyl)palladium complex. All involve rapid equilibrium formation of a π-olefin complex followed by (A) insertion of the palladium into the carbon-hydrogen bond, (B) removal of allylic hydrogen by a ligand on palladium, or (C) removal of allylic hydrogen by an external base. Kinetic studies with Na_2PdCl_4 in AcOH which show first-order dependence on the concentrations of both the olefin and $PdCl_4^{2-}$, but no dependence on acetate, are taken to be inconsistent with mechanisms involving allylic proton abstraction by external acetate. Product isotope effects for reactions of 2,2-dideuteriomethylenecyclohexane of 4.55 ± 0.1 in DMF and ca. 3.5 in AcOH at 60 °C are considered inconsistent with mechanisms involving Pd insertion into the allylic C-H bond. Literature crystal structures for 21 Pt-olefin complexes were found to possess close contacts between chloride ligands and allylic hydrogens, usually less than the sum of the van der Waals radii. These findings are taken to support a mechanism in which chloride ligand in the intermediate π-olefin complex abstracts an allylic proton to give the π-allyl complex. Calculations of deuterium isotope effects based on transition-state structures for the three mechanisms considered are also most consistent with the intramolecular proton removal by a chloride ligand.

The use of transition-metal complexes to cleave and functionalize C-H bonds is a mechanistically interesting and synthetically attractive process which has received considerable attention in recent years.[1] An early example of a useful C-H bond cleavage by a transition-metal complex is removal of an allylic hydrogen from an olefin on reaction with a Pd(II) salt to provide a (π-allyl)palladium complex, as shown in Scheme I. While general preparative procedures have been developed, few details of the

Scheme I. Formation of (π-Allyl)palladium Complexes from Olefins and Palladium(II) Salts



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