Figure 4. The change of nuclear configuration, displacement vector, and energy along the reaction coordinate of the substitution mode. The solid line is for reaction III and the dashed line is for reaction IV. Others are the same as in Figure 2.

on the width of potential barrier becomes important when the tunneling effect is discussed. The tunneling is expected not to be negligible near the top of the potential barrier even in the polyatomic reaction.

Many calculations of the trajectories of chemical reactions have been performed and afforded valuable information with respect to dynamic features of reactions.[12] Wang and Karplus[13] applied the trajectory method to the quantum mechanical surface. The trajectory, nevertheless, depends on the initial condition chosen. The intrinsic reaction coordinate is independent of the initial condition and is uniquely determined for a given reaction path on a given potential surface.

Applications of the intrinsic reaction coordinate to the dynamic problems of polyatomic reacting systems also have some advantages. The reaction coordinate automatically includes the reduced mass of the reacting system, and we can easily construct the equation of motion or the Hamiltonian of the system with considering the coordinate system perpendicular to the reaction coordinate. As shown in the present calculation, the effect of isotopic nuclei is directly realized in the width of the potential barrier. An application to the dynamics of polyatomic systems will be presented in the near future.

References and Notes

(1) For instance, see (a) R. Hoffman, R. Gleiter, and F. B. Mallory, *J. Am. Chem. Soc.*, **92**, 1460 (1970); (b) M. J. S. Dewer and M. C. Kohn, *ibid.*, **94**, 2704 (1972); (c) P. Marlet, S. D. Peyerimhoff, R. J. Buenker, and S. Shin, *ibid.*, **96**, 959 (1974); (d) K. Morokuma and R. E. Davis, *ibid.*, **94**, 1060 (1972).
(2) K. Fukui, *J. Phys. Chem.*, **74**, 4161 (1970).
(3) K. Fukui in "The World of Quantum Chemistry", R. Daudel and B. Pullman, Ed., D. Reidel Publishing Co., Dordrecht, Holland, 1974, p 113.
(4) K. Fukui, S. Kato, and H. Fujimoto, *J. Am. Chem. Soc.*, **97**, 1 (1975).
(5) R. A. Marcus, *J. Chem. Phys.*, **49**, 2610, 2617 (1968).
(6) (a) R. Wolfgang, *Prog. React. Kinet.*, **3**, 97 (1965); R. Wolfgang, *Acc. Chem. Res.*, **2**, 248 (1969); **3**, 48 (1970); (b) R. W. Walker, *J. Chem. Soc. A*, 2391 (1968); (c) M. J. Kurylo and R. B. Timmons, *J. Chem. Phys.*, **50**, 5113 (1969); (d) C. C. Chou and F. S. Rowland, *ibid.*, **50**, 2763, 5133 (1969).
(7) C. Eckart, *Phys. Rev.*, **47**, 552 (1935).
(8) L. M. Raff, *J. Chem. Phys.*, **60**, 2220 (1974).
(9) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970.
(10) M. J. D. Powell, *Compt. J.*, **7**, 155 (1964).
(11) S. Gill, *Proc. Cambridge Philos. Soc.*, **47**, 96 (1951).
(12) For instance, see (a) M. Karplus, R. N. Porter, and R. D. Sharma, *J. Chem. Phys.*, **43**, 3259 (1965); (b) D. L. Bunker and M. D. Pattengill, *ibid.*, **52**, 3041 (1970); T. Valencich and D. L. Bunker, *ibid.*, **61**, 4161 (1974).
(13) I. S. Y. Wang and M. Karplus, *J. Am. Chem. Soc.*, **95**, 8060 (1973).

Shigeki Kato, Kenichi Fukui*

Faculty of Engineering, Kyoto University
Sakyo-ku, Kyoto, Japan

Geometries of Nitrilium Betaines. The Clarification of Apparently Anomalous Reactions of 1,3-Dipoles

Sir:

Frontier molecular orbital (FMO) theory correctly rationalizes the regioselectivity of most 1,3-dipolar cycloadditions,[1] and successfully predicts regioselectivity in others.[1c,2] Previous generalizations about the frontier MO's of 1,3-dipoles, based on a variety of calculations using linear or planar geometries, are summarized in Figure 1. For unsymmetrical 1,3-dipoles, Z is always predicted to be the more nucleophilic terminus, and X the more electrophilic terminus.[3,4] However, using these generalizations, regioselectivity predictions for the HOMO controlled[1c,5] cycloadditions of nitrile ylides are incorrect. We concluded that "this case can only be rationalized by assuming that the calculations give the wrong result; this is, the larger [HOMO] coefficient must be on the "neutral" carbon (X in Figure 1)."[1c] Using this ad hoc assumption, regioselectivity data known at the time were rationalized,[5,6] and subsequent experimental work supported this unorthodox prediction of a theoretical result from experimental data.[7-9]

Optimizations of the geometries of the parent nitrilium betaines by ab initio LCAO-MO-SCF calculations,[10-13] reported here, indicate that the geometries of nitrile ylide and, to a lesser extent, of the imine are appreciably different from those commonly accepted.[14] Figure 2 shows the optimized geometries and a second geometry of interest for each species. The HCN-bent nitrile ylide geometry is favored over the planar, but otherwise optimized, geometry by 11.1 kcal/mol. Thus, this species resembles a bent allenyl anion rather than a planar propargyl anion,[15] By contrast, the linear structure is favored for fulminic acid, in fair agreement with experi-
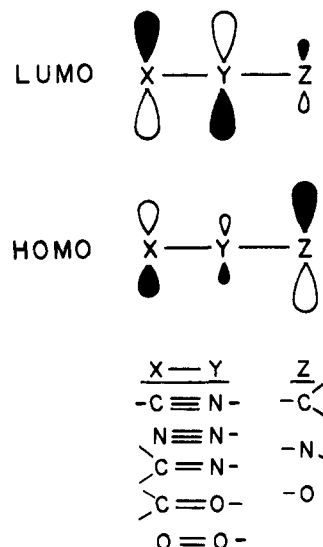

Figure 1. Frontier molecular orbitals of linear and planar 1,3- dipoles.
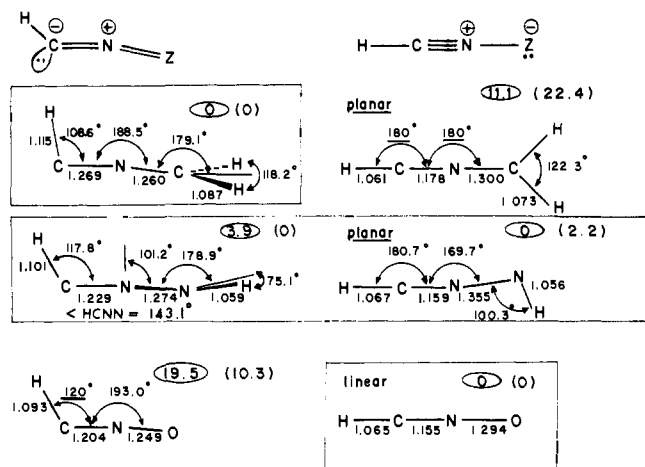
Figure 2. Optimized geometries of the nitrilium betaines. Angles fixed in any of the calculations are underlined. Circle energies are 4-31G; energies in parentheses are STO-3G.
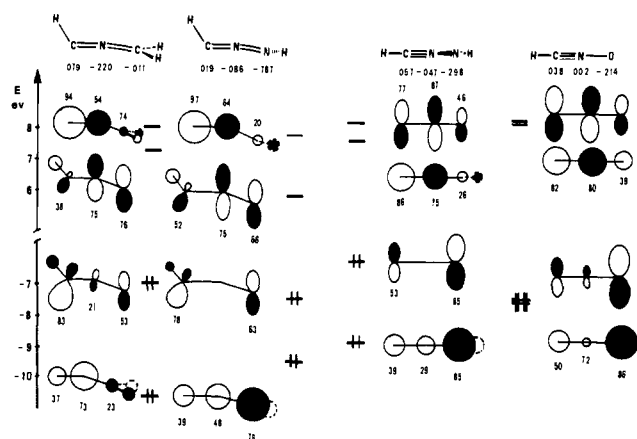

Figure 3. Frontier molecular orbitals (STO-3G) of nitrilium betaines. Numbers under structure are STO-3G charges, and those under orbitals are absolute values of coefficients.

ment,[16-18] and is 19.5 kcal/mol more stable than the molecule with a 120° HCN angle.

Nitrile imine is a flexible molecule, indeed. The STO-3G minimum is bent, resembling the optimized nitrile ylide, but with some bending of N-3 away from the HCN plane.[29] At the 4-31G level, a planar molecule, with moderate CNN bending, is preferred by 3.9 kcal/mol. The optimized molecule with a linear HCNN group is only 1.0 kcal/mol higher in energy than the planar 4-31G minimum.

The increasing stability of the planar geometry relative to the bent, as the electronegativity of the Z terminus increases, must arise from the fact that planar structures place more negative charge at Z and have less N-Z double bond character than HCN bent structures. The preference for HCN bending with decreasing electronegativity of Z can be understood in orbital terms. Thus, the planar ylide has a very high-lying HOMO which is substantially stabilized (2.04 eV) upon bending by mixing with vacant σ^* orbitals. An orbital mainly σ^*_{CH} in character is low-lying and will overlap well with the HOMO upon bending. Along the series from ylide to oxide, the HOMO decreases in energy and becomes more localized at the heteroatom, Z. Thus, bending results in less mixing of the HOMO with σ^* orbitals, and this lesser stabilization is compensated in the imine and overriden in the oxide by the loss of π bonding in the lowest allylic type MO upon bending.[19]

Figure 3 shows the FMO's and gross heavy atom atomic charges for the optimized geometries. The nitrile ylide HOMO is heavily concentrated at C-1, but still resembles the normal

three-orbital, four-electron system present in other 1,3-dipoles so that concerted cycloadditions can still occur. However, because of the bent geometry, C-1 is the nucleophilic terminus of nitrile ylides rather than C-3 as was found for the planar geometry. Thus, the regioselectivity of the cycloadditions to electron-deficient alkenes,[5-9] where C-1 of the ylide adds to the most electrophilic alkene terminus, is adequately accounted for, as is the site of protonation.[7]

The bent geometry of the ylide also resolves another anomaly. Because of their high nucleophilicities, nitrile ylides generally undergo reactions with their precursors, dimerize, or isomerize faster than they undergo reactions with electron-rich alkenes.[5,20] However, Padwa and co-workers recently reported that electron-rich double bonds undergo intramolecular attack on C-1 of photochemically generated nitrile ylide moieties to give zwitterionic intermediates which subsequently close to 1,3-dipolar cycloadducts or carbene-type cycloadducts.[9b] In these intramolecular reactions, attack by the alkene is constrained to occur perpendicular to the HCNC plane of the ylide. The second LUMO (SLUMO), which is perpendicular to the HCNC plane, is low-lying and presents a large vacancy at C-1 for attack by the more nucleophilic terminus of an alkene, without the possibility of simultaneous bonding at the C-3. In fact, the HOMO and SLUMO have an uncanny resemblance to the HOMO and LUMO of a singlet carbene. Thus, these reactions, as well as thermal 1,4-hydrogen shifts from C-3 alkyl groups to C-1,[21] are accounted for adequately by the ground state orbitals of the bent nitrile ylide. No second geometrical ground state minimum for nitrile ylides is required, and none are found computationally.

Placing electron-withdrawing groups at C-3, like the substitution of O for CH_2, should favor planarization of nitrile ylides. For example, bis(trifluoromethyl)benzonitrile ylide adds alcohols and electron-deficient alkenes with regioselectivity which indicates that the $C(CF_3)_2$ terminus is most nucleophilic,[22] as expected from considerations of the FMO's of a planar ylide.[1] C-3 of benzonitrile cyclopropylide is also the more nucleophilic terminus,[23] compatible with the notion that the effective electronegativity and resistance to planarization of the cyclopropyl anion terminus causes the HCNC group to be linear, with pyramidalization about C-3.[24]

The shapes and energies of the FMO's of fulminic acid are as discussed previously,[1,4] so that the oxygen terminus is the most nucleophilic site, the carbon terminus the most electrophilic. These FMO's probably overestimate the relative nucleophilicity of the O terminus, because HCN bending is not energetically difficult.[16] Cycloaddition transition states have appreciable HCN and CNO bending,[25] which increases the relative nucleophilicity of the C terminus and, to a lesser extent, the electrophilicity of the O terminus. The lesser tendency of nitrile oxides to give 4-substituted adducts with very electron-deficient alkenes than is observed with nitrones,[26] may be partially accounted for in this way.

Figure 3 shows the FMO's of both the optimum and planar geometries of nitrile imine. The drastic changes in FMO energies and shapes with energetically easy geometrical distortions suggest that the preferred geometry of approach of nitrile imine to a reagent will be dictated by the electronic characteristics of the reagent. Electrophilic reagents will promote imine planarity, which raises the HOMO energy and facilitates stabilization of the transition state by increasing mixing with the electrophile LUMO, and nucleophilic reagents will promote bending, since this causes a drastic lowering of the imine LUMO. The results of these calculations suggest that FMO's of an assumed (even the optimized) geometry may not be valid reactivity predictors if easy molecular distortions, which result in drastic FMO changes, can occur.[27]

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References and Notes

(1) (a) K. N. Houk, *J. Am. Chem. Soc.*, **94**, 8953 (1972); (b) K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *ibid.*, **95**, 7287 (1973); (c) K. N. Houk, J. Sims, C. R. Watts, and L. J. Luskus, *ibid.*, **95**, 7301 (1973); (d) K. N. Houk, *Acc. Chem. Res.*, **8**, 361 (1975).
(2) J. Sims and K. N. Houk, *J. Am. Chem. Soc.*, **95**, 5798 (1973).
(3) The nucleophilic terminus is that with greater negative charge and highest HOMO coefficient; the electrophilic terminus has largest LUMO coefficient and the least negative (or most positive) charge.[1b,c,4]
(4) MINDO/2 and MINDO/3 optimized geometries: P. Caramella, R. W. Gandour, J. A. Hall, C. G. Deville, and K. N. Houk, *J. Am. Chem. Soc.*, in press. These calculations also predict the trends obtained here by ab initio techniques: in MINDO/3 (MINDO/2) the HCN angles are 116° (114°), 126° (122°), and 159° (150°) for the ylide, imine, and oxide, respectively. The linear nitrile oxide is only 0.1 (0.2) kcal/mol higher in energy than the bent.
(5) A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, Jr., *J. Am. Chem. Soc.* **95**, 1945, 1954 (1973).
(6) R. Huisgen, *Helv. Chim. Acta*, **50**, 2421 (1967); K. Bunge, R. Huisgen, R. Raab, and H. J. Sturm, *Chem. Ber.*, **105**, 1307 (1972), and references therein; B. Jackson, M. Marky, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, **55**, 919 (1972).
(7) A. Padwa and J. Smolanoff, *J. Chem. Soc., Chem. Commun.*, 342 (1973).
(8) N. Gakis, H. Heimgartner, and H. Schmid, *Helv. Chim. Acta*, **58**, 748 (1975), and references therein.
(9) (a) A. Padwa and S. I. Wetmore, Jr., *J. Am. Chem. Soc.*, **96**, 2414 (1974); (b) A. Padwa and P. H. J. Carlsen, *ibid.*, **97**, 3862 (1975); A. Padwa, A. Ku, A. Mazzu, and S. I. Wetmore, Jr., *ibid.*, **98**, 1048 (1976); A. Padwa and P. H. J. Carlsen, submitted for publication.
(10) The GAUSSIAN 70 series of programs was used: W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. The optimizations were carried out by variations of all geometrical parameters by the procedure described by Pople,[11] using the minimal STO-3G basis set,[12] while energies of optimized geometries were recalculated using the split-valence 4-31G basis set.[13,14] See W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Prog. Phys. Org. Chem.*, **11**, 175 (1974), for extensive comparisons of the results of this methodology with experiment.
(11) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).
(12) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
(13) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **54**, 724 (1971).
(14) (a) R. Huisgen (*Angew. Chem., Int. Ed. Engl.*, **2**, 633 (1963)) postulated that the HCN-bent geometries of nitrilium betaines would be less stable than the planar, because allyl resonance would be maximum for the planar geometries. (b) L. Salem (*J. Am. Chem. Soc.*, **96**, 3486 (1974)) has discussed the photochemical ring-opening of azirines and mentions the possibility of initial formation of a diradical (bent) species which may undergo reactions different from the dipolar (linear) species. Padwa has suggested that the stable linear geometry can undergo rehybridization to a higher energy bent (carbene) form, which may undergo carbene-like cycloadditions.[9]
(15) STO-3G calculations on the allenyl-propargyl anion system indicate the following geometries (relative energies): propargyl (planar), r_{HC_1} = 1.05 Å, $r_{C_1C_2}$ = 1.19 Å, $r_{C_2C_3}$ = 1.37 Å, r_{C_3H} = 1.07 Å, $\angle HC_3H$ = 116.4°, (E_{rel} = +6 kcal/mol); allenyl (nonplanar); r_{HC_1} = 1.10 Å, $r_{C_1C_2}$ = 1.26 Å, $r_{C_2C_3}$ = 1.33 Å, r_{C_3H} = 1.08 Å, $\angle HC_3H$ = 113.8°, $\angle H_1C_1C_2$ = 115.8° (E_{rel} = 0). This energy difference is reduced to 5 kcal/mol in 4-31 G calculations.
(16) Although microwave data on fulminic acid were originally interpreted in terms of a linear geometry (r_{HC} = 1.027 Å; r_{CN} = 1.168 Å; r_{NO} = 1.199 Å),[17] recent ir data imply that this molecule is "quasi-linear", with the linear geometry ~0.1 kcal/mol less stable than a bent species ($\angle HCN$ = 165°; r_{HC} = 1.060 Å; r_{CN} = 1.168 Å; r_{NO} = 1.199 Å).[18] Although the STO-3G calculations do not reproduce this hump at the bottom of the surface, the flatness of the HCN bending surface is reproduced: the optimized molecule with $\angle HCN$ = 165° is only 1.4 kcal/mol (4-31G) less stable than the linear. MINDO/3 calculations reproduce this hump quantitatively[4]
(17) H. K. Bodenseh and K. Winnewisser, *Z. Naturforsch.*, **24**, 1973 (1969).
(18) B. P. Winnewisser, M. Winnewisser, and F. Winther, *J. Mol. Spectrosc.*, **51**, 65 (1974).
(19) Similar reasoning has been used to rationalize inversion barriers in AH_3 molecules: W. Cherry and N. Epiotis, *J. Am. Chem. Soc.*, **98**, 1135 (1976).
(20) R. Huisgen, R. Sustmann, and K. Bunge, *Chem. Ber.*, **105**, 1324 (1972).
(21) L. A. Wendling and R. G. Bergman, *J. Am. Chem. Soc.*, **96**, 308 (1974); A. Demoulin, H. Gorissen, A.-M. Hesbain-Frisquen, and L. Ghosez, *J. Org. Chem.*, **41**, 83 (1976); *J. Am. Chem. Soc.*, **97**, 4409 (1975).
(22) K. Burger, W. Thenn, and E. Müller, *Angew. Chem., Int. Ed. Engl.*, **12**, 155 (1973); K. Burger, and K. Einhellig, *Chem. Ber.*, **106**, 3421 (1973); K. Burger, K. Einhellig, G. Süss, and A. Gieren, *Angew. Chem., Int. Engl.*, **12**, 156 (1973).
(23) A. Padwa and J. K. Rasmussen, *J. Am. Chem. Soc.*, **97**, 5912 (1975).
(24) Nitrile yields have now been observed spectroscopically in glasses at low temperature: A. Orahovata, H. Heimgarten, H. Schmid, and W. Heinzelmann, *Helv. Chim. Acta*, **58**, 2662 (1975).
(25) D. Poppinger, *J. Am. Chem. Soc.*, **97**, 7486 (1975).
(26) K. N. Houk, J. Sims, and Y.-M. Chang, unpublished results.
(27) Although one cannot be sure that calculations with more extended basis sets, such as are necessary for anion calculations (J. W. Williams, Jr., and A. Streitweiser, Jr., *J. Am. Chem. Soc.*, **97**, 2634 (1975)), and with inclusion of correlation energy (for limited CI calculations on some 1,3-dipoles, see E. F. Hayes and A. K. Q. Siu, *J. Am. Chem. Soc.*, **93**, 2090 (1971)), will continue to favor a particular geometry shown, the trends observed here are expected to be preserved in more extensive calculations, as they are also in MINDO/2 and MINDO/3 calculations.[4]
(28) (a) On leave from the University of Pavia, Italy; (b) Camille and Henry Dreyfus Teacher–Scholar Grant Recipient, 1972–1977; Fellow of the Alfred P. Sloan Foundation, 1975–1977.
(29) A previous partial optimization of nitrile imine by ab initio techniques gave $\angle HCN$ = 107°, $\angle NNH$ = 115°, r_{CN} = 1.34 Å, and r_{NN} = 1.33 Å: B. T. Hart, *Aust. J. Chem.*, **26**, 461 (1973).

Pierluigi Caramella,[28a] **K. N. Houk***[28b]

Department of Chemistry, Louisiana State University
Baton Rouge, Louisiana 70803
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Cyclization and Rearrangement in the Reaction of Allylbis(dimethylglyoximato)cobalt(III) Complexes with Tetracyanoethylene. Crystal Structure of *trans*-3,3,4,4-Tetracyano-2-phenylcyclopentylbis-(dimethylglyoximato)imidazolecobalt(III)

Sir:

Mainly because of their biological analogues, 1,2-rearrangements[1] are of considerable importance in organocobalt chemistry. Indeed, despite appreciable efforts to understand 1,2-migrations of functional groups catalyzed by adenosylcobalamin, they are not understood at all[2] and present theories have had to rely almost exclusively on results from synthetic "model" systems. We here describe a further example of a 1,2-rearrangement in organocobaloxime chemistry which also has analogues in the organic chemistry of other organometallic complexes.[3]

Several allylbis(dioximato)pyridinecobalt(III) complexes (e.g., **1**) react with tetracyanoethylene (**2**) in dichloromethane to give 3,3,4,4-tetracyanocyclopentylbis(dioximato)pyridinecobalt(III) complexes (e.g., **3**). Thus, allylbis(dimethylglyoximato)pyridinecobalt(III) (**1a**) gives a near quantitative yield of **3a** (eq 1), but the yield of cyclic product from 3-substituted allyl complexes **1b**, **1c** and **1e** is lower[5] (40–70%) and that from the 2-substituted allyl complex **1d** is negligible.

The ^1H NMR spectra and chromatographic behavior of the products from **1b**, **1c** and **1e** indicate that only a single cyclic product is formed in each case and the solid (**3e**) obtained from
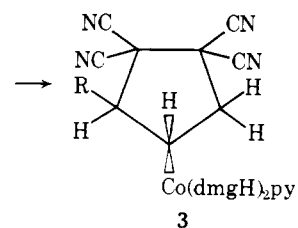
$$RCH{=}CR'CH_2Co(dmgH)_2B \; + \; (NC)_2C{=}C(CN)_2$$
$$\mathbf{1} \qquad\qquad\qquad\qquad \mathbf{2}$$
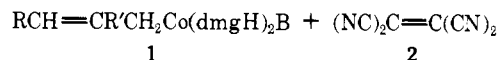
1a, R = R′ = H; B = py
1b, R = Me; R′ = H; B = py
1c, (trans)R = Ph; R′ = H; B = py
1d, R = H; R′ = Me; B = py
1e, (trans)R = Ph; R′ = H; B = imidazole

(1)

3a, R = H; B = py
3b, R = Me; B = py
3c, R = Ph; B = py
3e, R = Ph; B = imidazole