barriers for guanidinium and amidinium. We have provided a rationale for the unusual basicity and stability of guanidine and a working model to understand the effects of substituents (BH_2, CH_3 NH_2, OH, and F) on ionic centers.

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(26) To be consistent, we used the experimental geometry for each molecule, keeping the rest of the molecule fixed when we removed a proton. That this is not too bad an approximation is evident when one compares the geometry of CH_4 (r = 1.09 Å, θ = 109.5°) with that predicted for CH_3^- by R. Kari and I. Czimadia, *J. Chem. Phys.*, **50**, 1443 (1969) (r = 1.12 Å, θ = 105°). In any case, the relative energies should probably be more accurate than their absolute value. We did not examine the relative energies of isomeric species; for example, CH_3O^- is likely to be comparable in stability to $^-CH_2OH$.

An *ab Initio* Molecular Orbital Study of Ethylenedione (O=C=C=O)

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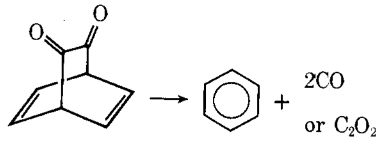
Abstract: *Ab initio* molecular orbital theory with minimal (STO-3G) and split-valence (4-31G) basis sets has been used to study ethylenedione (O=C=C=O) at the real and complex single determinant and configuration interaction levels. The linear (forbidden) and trans (allowed) dissociative pathways leading to two molecules of carbon monoxide have been examined in detail, their differences clearly delineated and found to be in accord with orbital symmetry requirements. It is shown that ethylenedione is kinetically (singlet) and thermodynamically (singlet and triplet) unstable with respect to two molecules of carbon monoxide. This result is consistent with experimental evidence but contrasts with the findings of previous theoretical studies.

Recently, ethylenedione (**1**) has become the subject of much experimental[2] and theoretical[3,2c] interest.

O=C=C=O

1

Experimentally, attention has focussed on the possibility of generating ethylenedione by thermal decomposition of molecules such as the bicyclo[2.2.2]octadienones (**2**).[2] It now appears that this reaction, which proceeds with difficulty, in contrast to the decomposition of bicyclo[2.2.1]heptadienones[4] (**3**), occurs by stepwise loss of CO, rather than by the concerted elimination of ethylenedione. That the involvement of **1** in this reaction is likely to be transitory at best is supported by a number of observations. All attempts to trap **1** have been unsuccessful (although CO has been de-



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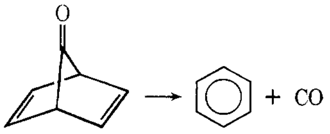

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Table I. Structures and Energies of Carbon Monoxide (CO) and Linear Ethylenedione (C_2O_2)

			Bond length, Å		Energies	
Species	Electronic state	Level of calculation	C–C	C–O	Total, hartrees	Relative to 2CO, kcal mol^{-1}
CO	$^1\Sigma^+$	STO-3G/R		1.146[a]	−111.22545[a]	
		4-31G/R		1.128	−112.55236	
		Exptl		1.128[b]		
	$^3\Pi$	4-31G/UHF		1.240	−112.38515	
		Exptl		1.209[b]		
C_2O_2	$(^1\Sigma_g^+)$	STO-3G/R	1.267	1.211	−222.32040	81.9
		4-31G/R	1.269	1.184	−224.98516	75.0
	$^1\Delta_g$	STO-3G/C	1.264	1.211	−222.33546	72.4
		4-31G/C	1.267	1.184	−224.99736	67.4
		STO-3G/CI (S)	1.267	1.210	−222.33315	75.7
		STO-3G/CI (L)	1.257	1.220	−222.38868	
	$^1\Sigma_g^+$	STO-3G/CI (S)	1.272	1.210	−222.30925	90.4
	$^3\Sigma_g^-$	STO-3G/UHF	1.256	1.214	−222.37464	47.9
		4-31G/UHF	1.261	1.186	−225.03124	46.1
C_2O_2	Singlet–triplet separation	STO-3G			24.5 kcal mol^{-1}	
		4-31G			19.3 kcal mol^{-1}	

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tected), and the products from the reactions are suggestive of radical intermediates. Furthermore the photodecomposition of **2** in solution or in the solid state[1cd] leads smoothly to the aromatized molecule and CO. Similarly, the dianion of the dibenzo derivative of **2** readily decomposes to give anthracene as one of the products.[5]

Previous theoretical treatments[3] have found that linear ethylenedione has a triplet ground state. Differing conclusions have been reached concerning the singlet potential surface both with regard to the existence of a potential minimum for linear ethylenedione and also with regard to the energy difference between such a structure and two separated CO molecules. These will be discussed in detail below.

In this paper, we report the results of an *ab initio* molecular orbital study of ethylenedione in which we have employed real and complex single determinant and configuration interaction (CI) treatments.

Methods

Single determinant calculations were carried out using standard *ab initio* LCAO-SCF molecular orbital theory with both real (restricted[6] [STO-3G/R, 4-31G/R] for closed shells and unrestricted[7] [STO-3G/UHF, 4-31G/UHF] for open shells) and complex[8] [STO-3G/C, 4-31G/C] molecular orbitals. The Gaussian 70 system of programs was employed[9] together with a complex self consistent field routine written by Dr. D. P. Miller.

The CI calculations follow the same lines as those in a recent study of the excited states of HCN.[10] The CI wave function includes all single excitations from a set of reference configurations which, from simple molecular orbital arguments, have to be included to describe the state of interest properly, or, which were found to be important in test calculations. In a "small" CI calculation [STO-3G/CI (S)], the reference configurations were $\ldots(2\pi_u(x))^2$, $\ldots(2\pi_u(y))^2$, and $\ldots(5\sigma_u)^2$. The first two configurations were needed to describe the $^1\Sigma_g^+$ state of linear C_2O_2 and one component of the $^1\Delta_g$ state, whereas the third configuration dominates the $^1\Sigma_g^+$ wave function at very large C–C distances. In a larger CI calculation [STO-3G/CI (L)], four additional reference configurations were included which turned out to have large coefficients in the $^1\Delta_g$ wave function. These configurations correspond to double excitations from $1\pi_g$ to $2\pi_u$ and from $2\pi_u$ to $2\pi_g$. For the Δ state, the iterative natural orbital method[11] was employed to arrive at an optimum set of orbitals. Usually, four or five cycles were required to stabilize the energy to 10^{-4} hartree. The CI programs were written by one of us (D.P.).

Calculations were performed with both the minimal STO-3G[12] and split-valence (extended) 4-31G[13] basis sets. These basis sets have been used extensively in calculations of molecular geometries[14,15] and molecular energetics.[13,15,16]

Results and Discussion

Simple molecular orbital considerations suggest that the low-lying states of linear C_2O_2 are derived from the configuration

$$(\sigma_g)^{10}(\sigma_u)^8(1\pi_g)^4(1\pi_u)^4(2\pi_u)^2$$

Two electrons occupying the two orthogonal π molecular orbitals $2\pi_u(x)$ and $2\pi_u(y)$ give rise to three states: $^3\Sigma_g^-$, $^1\Delta_g$, and $^1\Sigma_g^+$. Basically the same situation is found in the molecular orbital description of oxygen, where the lowest electronic state is the triplet $^3\Sigma_g^-$ and the first excited state is $^1\Delta_g$.

Conventional single determinant molecular orbital theory does not adequately describe the electronic structure of the singlet states of molecules with partially filled sets of degenerate or near-degenerate orbitals. In the case of linear singlet C_2O_2 (with the molecular axis in the z direction), the interaction of at least two determinants

$$D_1 = |\ldots 2\pi_u(x)2\pi_u(x)|$$

$$D_2 = |\ldots 2\pi_u(y)2\pi_u(y)|$$

must be taken into account, leading to a wave function of the form

$$\Psi = 2^{-1/2}(D_1 \pm D_2)$$

The positive sign is associated with a $^1\Sigma_g^+$ state, the negative sign with one component of a $^1\Delta_g$ state. The essential features of this two-determinant treatment can be reproduced by single-determinant molecular orbital theory if the orbitals are allowed to become complex. The two components of the $^1\Delta_g$ state for linear C_2O_2 correspond to configurations in which the last two electrons are assigned with antiparallel spins to complex molecular orbitals $\pi_u(x) + i\pi_u(y)$ or to $\pi_u(x) - i\pi_u(y)$. Despite the limitations mentioned above, we have carried out some single determinant

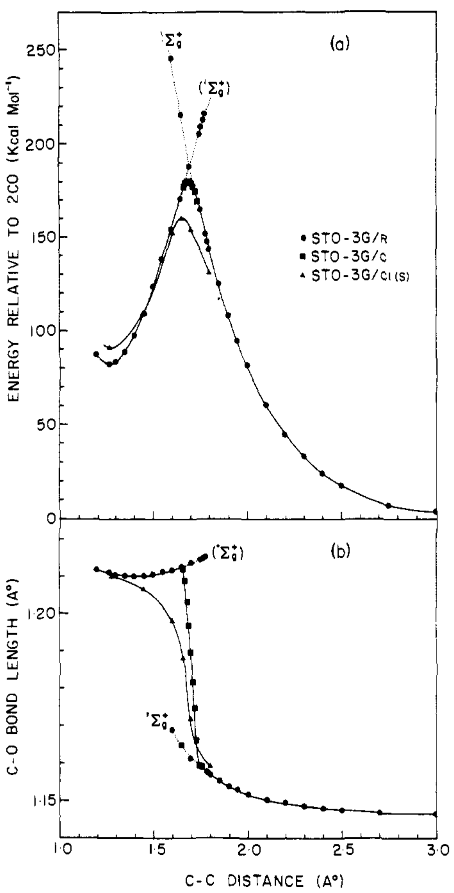

Figure 1. Linear ($D_{\infty h}$) dissociation of ethylenedione: (a) calculated relative energies; (b) calculated C–O bond lengths.

calculations for linear ethylenedione in which the molecular orbitals are constrained to be real for comparison with the complex and CI results. In these cases, the procedure does not yield fully symmetry-adapted wave functions and the electronic states are denoted by ($^1\Sigma_g{}^+$).

Our detailed results for the low-lying states of linear C_2O_2 and the ground state of CO are presented in Table I. The optimized geometries show C═C lengths (1.264 Å, STO-3G/C) slightly shorter and C═O lengths (1.211 Å, STO-3G/C) slightly longer than normal C═C double bonds (1.288 Å, STO-3G in allene;[17] 1.300 Å, STO-3G in ketene[18]) and C═O double bonds (1.188 Å, STO-3G in carbon dioxide;[14] 1.183 Å, STO-3G in ketene[18]), respectively. These results are consistent with the occupation of the $2\pi_u$ (C–C bonding, C–O antibonding) orbitals. It is interesting to note that the theoretical geometries for the singlet and triplet states are virtually identical.

The structure of lowest energy for linear ethylenedione is the triplet $^3\Sigma_g{}^-$ with a valence shell electronic configuration $(3\sigma_g)^2(3\sigma_u)^2(4\sigma_g)^2(5\sigma_g)^2(1\pi_u)^4(1\pi_g)^4(2\pi_u)^2$. However, when comparing the energies of the triplet and singlet states, it must be borne in mind that the unrestricted Hartree–Fock procedure used in this study preferentially stabilizes triplets compared with singlets. For example, the 4-31G singlet–triplet energy difference for methylene calculated[19] using the same procedure as above is 40 kcal mol^{-1} whereas the best available theoretical[11b,20] and experimental[21] estimates suggest 8–11 kcal mol^{-1}. Because of the relatively small singlet–triplet energy differences (19.3 kcal mol^{-1} with 4-31G) calculated in the present work, it therefore remains uncertain whether the ground state of linear ethylenedione is a singlet or a triplet.

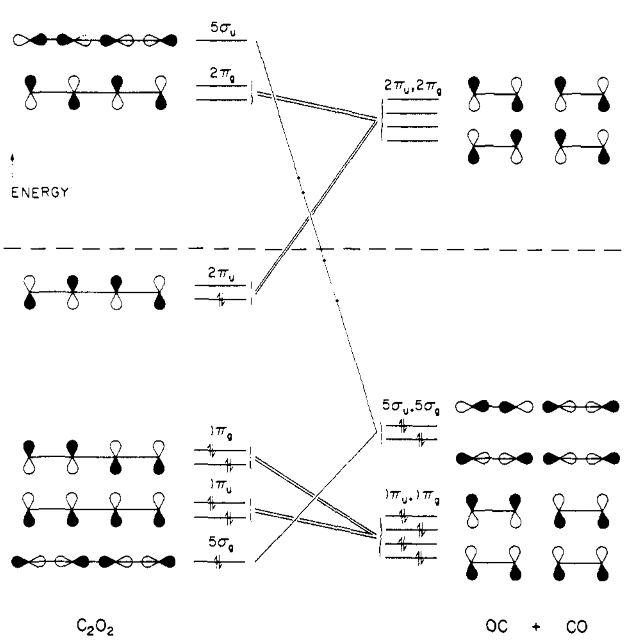

Figure 2. Correlation diagram for linear ($D_{\infty h}$) dissociation of ethylenedione. Degenerate orbitals are bracketed together and only one of each of the degenerate π_x, π_y pairs is shown.

Both the singlet and triplet states of linear ethylenedione are found to have considerably higher energy than separated molecules of CO in their ground singlet state. For the $^1\Delta_g$ state, this energy is about 70 kcal mol^{-1} while for $^3\Sigma_g{}^-$ it is approximately 50 kcal mol^{-1}. For the triplet state of C_2O_2, an additional energy comparison which is of interest is with $^1\Sigma$ CO + $^3\Pi$ CO and here we find the $^3\Sigma_g{}^-$ state of C_2O_2 lower in energy by 60 kcal mol^{-1}.

For singlet ethylenedione, we have examined two possible distortions from the optimum linear structure. In the first place, we have examined the linear dissociation to two molecules of CO (Figure 1). The molecule was constrained to be linear ($D_{\infty h}$)[22] and the C–O bond length optimized for each value of the reaction coordinate (the C–C distance). As may be seen from the correlation diagram (Figure 2), the linear dissociation pathway is symmetry forbidden. The $5\sigma_u$ level, unoccupied in the low-lying states of linear ethylenedione, drops sharply with increasing C–C distance and decreasing C–C overlap, and finally correlates with the antibonding combination of the two carbon lone pair orbitals which are doubly occupied in the ground state of the fragment CO molecules. Not surprisingly, the activation energy for this process is found to be very high. For the STO-3G/C [STO-3G/CI (S)] calculation, the transition state lies 98.8 (69.5) kcal mol^{-1} above linear C_2O_2 and 180.7 (159.8) kcal mol^{-1} higher than two separated molecules of CO.

It is interesting to note that the potential energy curves for the reactant-like and product-like systems merge smoothly, providing the important configurations for both the reactant and the product are included in the calculation. This was accomplished here by use of the complex SCF procedure in which interactions between the orbitals $2\pi_u$ and $5\sigma_u$ are taken into account, and the normal configuration interaction treatment in which the dominant configuration in the wave function of the products, . . . $(5\sigma_u)^2$, is one of the reference configurations.

This monotonic behavior contrasts with results from previous studies of symmetry forbidden reactions, in which the potential curves from reactant and product did not meet, and the full potential surface had to be constructed to correctly study the reaction.[23] These latter reactions are characterized by large variations in other geometrical parameters accompanying small changes in the chosen reaction

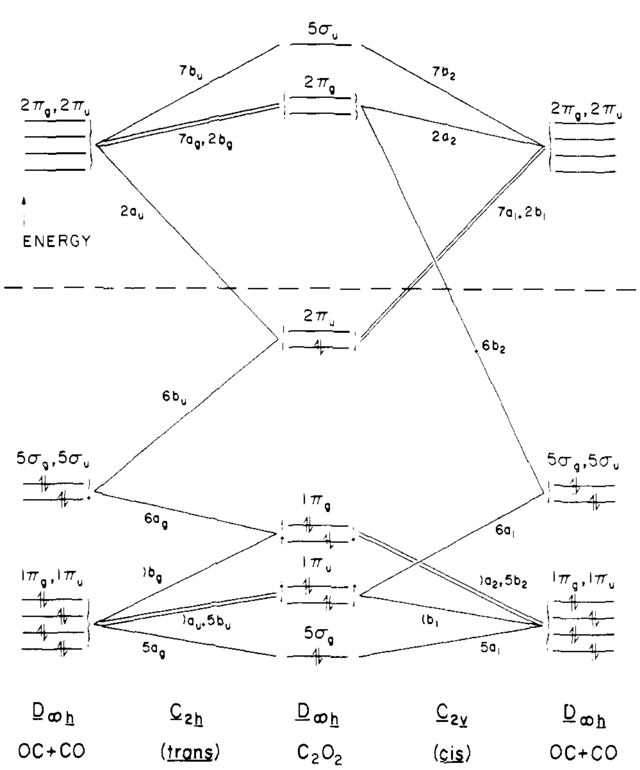

Figure 3. Correlation diagram for cis and trans bent ethylenedione. Degenerate orbitals are bracketed together.

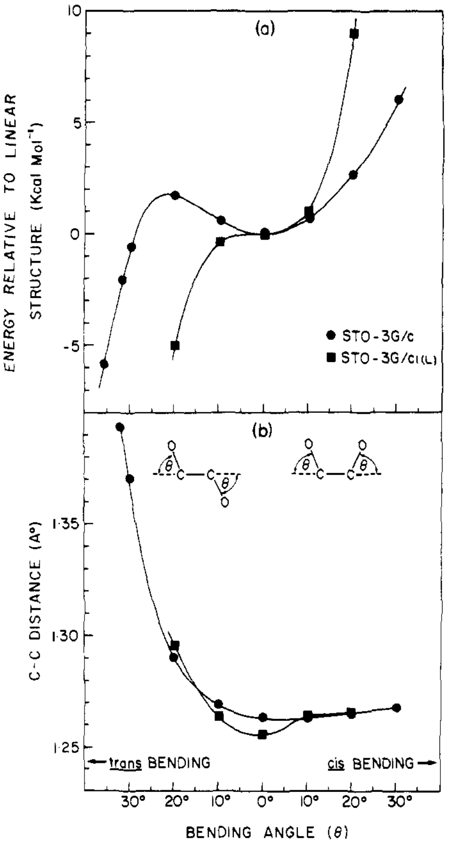

Figure 4. Bending of $^1\Delta_g$ state of linear ethylenedione: (a) calculated relative energies; (b) calculated C–C distances.

coordinate. On the other hand, in the linear ($D_{\infty h}$) dissociation pathway for ethylenedione, the only parameter which can vary is the C–O bond length and, as may be seen from Table I, it changes by only a few per cent over the entire transformation from C_2O_2 to 2CO. Accordingly, the "product valley" and the "reactant valley" on the C_2O_2 energy surface are displaced only slightly in the direction orthogonal to the reaction coordinate (*i.e.*, with respect to the C–O bond length), and passage occurs smoothly from one valley to the other. This seems to indicate the absence of *cul de sacs* at the end of the product and reactant valleys in this reaction.

The other distortion we have examined involves cis (C_{2v}) and trans (C_{2h}) bending of the C_2O_2 skeleton. The triplet state lies in a deep minimum with respect to these distortions (STO-3G/UHF). The behavior of the singlet state, however, is far more interesting. The correlation diagram (Figure 3) shows that cis bending does not remove the symmetry barrier to dissociation into two molecules of CO. In line with this qualitative prediction, our calculations show only a small increase in the C–C bond length and a marked increase in energy accompanying cis bending (see Figure 4). On the other hand, dissociation of trans bent ethylenedione is symmetry allowed; one of the crucial π levels ($2\pi_u$ in $D_{\infty h}$) now transforms as b_u and may develop smoothly into the antibonding combination of the two carbon lone pair orbitals of separated CO molecules.

The complex SCF calculations suggest that singlet ethylenedione lies in a shallow minimum with respect to bending. At the CI level, the barrier to trans bending disappears, but the curve still shows a point of inflection. In either case, it appears that singlet ethylenedione is unlikely to find a significant energy barrier to trans distortion and hence can circumvent the symmetry imposed barrier to linear dissociation. At a bending angle of 40°, the dissociation appears to be complete (STO-3G/C). We do not find a stable trans bent ethylenedione.

It is of interest to compare our results with those of previous theoretical work. Most qualitative and quantitative [INDO, EHT, and the previous *ab initio* calculations of Beebe and Sabin (denoted BS below)] studies have predicted that the ground state of ethylenedione is a linear triplet.[3] The singlet-triplet energy difference has been estimated at 18.6 kcal mol^{-1} (INDO)[3d] and 31.1 kcal mol^{-1} (BS).[3f] In marked contrast to our findings, *all* the previous quantitative studies find that ethylenedione is *more* stable than two molecules of CO. Estimates of this energy difference are 247 (CNDO/2),[3e] 259 (INDO),[3e] 3 (VEHT),[3e] 46 (MINDO/2),[3e] 21 (MINDO/3),[3g] and 55 kcal mol^{-1} (BS).[3f] Finally, in view of the flatness of the potential curve for singlet ethylenedione in the vicinity of the linear structure, it is not surprising that there is some disagreement in the literature concerning its structure. Thus, whereas CNDO/2,[3e] INDO,[3d,e] and EHT[3b] calculations predict a linear structure, VEHT,[3e] MINDO/2,[3e] and MINDO/3[3g] studies indicate a trans bent geometry for the singlet. These predictions are undoubtedly influenced by the very different (and in some cases, very poor) estimates that these methods give for the C_2O_2–2CO energy difference.

Because of the large differences between our results and those of the previous *ab initio* (BS) study,[3f] we carried out additional calculations using the BS basis set. This procedure led to a C_2O_2–2CO energy difference very close to our STO-3G and 4-31G values. We are therefore uncertain as to the reason for the discrepancy between the BS and our results.

Conclusions

The main conclusions that emerge from this systematic *ab initio* molecular orbital study of ethylenedione are as follows. (i) Triplet ethylenedione is linear and probably lies lower in energy than the linear singlet. (ii) Ethylenedione in all states is thermodynamically much less stable than separated ground state CO molecules. (iii) The linear dissociation of ethylenedione to two molecules of CO is symmetry forbidden and accordingly has a high activation energy. (iv) In contrast, dissociation of trans bent ethylenedione is symmetry allowed; trans bending leads easily to two separated molecules of CO with little or no activation energy. (v) Our results therefore suggest that it is unlikely that singlet ethylenedione will be observed experimentally. There is a somewhat better prospect for generating and observing the triplet.

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The Generalized Valence Bond Description of Allyl Radical[1a]

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Abstract: *Ab initio* generalized valence bond (GVB) and configuration interaction calculations are reported for the ground and low-lying excited states of allyl. The GVB wave functions lead to energies very close to those of the full CI wave functions (0.13 eV error for the ground state) providing a firm basis to the interpretations based on the GVB wave functions. We find that the ground state and first singlet excited state of allyl are well described as the classical resonant and antiresonant combinations of simple valence bond structures. The theoretical value obtained for the allyl resonance energy is 11.4 kcal, in reasonable agreement with thermochemical estimates (11.6 ± 2 kcal).

I. Introduction

The π orbitals of unsaturated organic compounds are chemically the most active part of the molecules and as such have been the subject for much theoretical investigation. In a previous paper,[2] we reported generalized valence bond (GVB) calculations on ethylene and allyl cation, including some excited states. In this paper we report GVB calculations on the ground and excited states of allyl radical, allowing simultaneous optimization of both the spatial orbitals and the spin coupling while generating a spin eigenfunction.[3-5]

The π-electron system of allyl cation is the smallest π system displaying what is known in valence bond (VB) theory as resonance. The GVB approach is well suited to describing resonance since the wave function is sufficiently flexible to describe a linear combination of the two classical resonance forms. However, in the GVB approach the shapes of the orbitals are optimized (rather than assumed to be atomic-like as in VB), and the overall form of the wave function is not restricted to expressions of the resonance form. Even so we find that the ground and first excited states are well described as the resonant and antiresonant states

thus providing a rigorous quantum mechanical basis for the concept of resonance.

II. Calculational Considerations

A. The Wave Functions. a. Hartree–Fock. The Hartree–Fock (HF) wave function for the ground state of allyl radical may be written in the form[6]

$$\mathcal{A}[\varphi_1\alpha\varphi_1\beta\ldots\varphi_q\alpha\varphi_q\beta\varphi_{\pi_1}\alpha\varphi_{\pi_1}\beta\varphi_{\pi_2}\alpha] \qquad (1)$$