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LETTER TO THE EDITOR

The dynamics around the glass transition in the spin density wave ground state of $\text{TMTSF}_2\text{PF}_6$

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Abstract. We present experimental observations of the dielectric and energy relaxations in the spin density wave state of $\text{TMTSF}_2\text{PF}_6$. These measurements reveal two distinct dynamical regimes. The dielectric relaxation shows a critical slowing down towards a 'static' glass transition around 2 K. Below this temperature very slow energy relaxation processes appear, which exhibit breaking of ergodicity associated with aging effects. These results are analysed within the framework of glass-forming systems.

The glass transition is one of the most investigated phenomena in solid-state physics because it occurs in many different glass-forming systems irrespective of their chemical and physical properties. It seems that these systems have common features, which suggest underlying universalities [1]. One of the recurring characteristics is that the elementary units responsible for the relaxation processes are coupled to each other. The loss of independence is caused by the mutual constraints between the elementary units, which requires the relaxation process to be highly cooperative [1]. Several different kinds of relaxation phenomenon have been identified in glass systems. An enormous increase of the viscosity upon cooling to the freezing temperature is manifested in the main, so-called α relaxation or primary relaxation. The corresponding relaxation time τ increases faster than activated, or Arrhenius, dependence and at certain temperatures (there are different definitions for the glass transition temperature) it becomes inaccessible for usual experimental time windows. Secondary, β (or Johari-Goldstein) relaxation [2] takes place at lower temperatures and it has activated behaviour. The activation energy for the β relaxation is much lower than any apparent activation energy obtained from the slope of α relaxation, so that in a frequency versus temperature plot the two will tend either to merge into a single relaxation region or else the β relaxation will cross the main relaxation at high frequencies and at high temperatures [2].

Density wave (DW) systems are possibly very good examples of glass-forming systems as they show many metastable states [3] and high cooperativity. The disorder in the DW ground state is caused by the randomly distributed impurities, which pin the DW phase. A broad distribution of relaxation times (or equivalently a broad distribution of pinning energies) has been revealed [4] in the dielectric relaxation measurements of charge-density waves (CDWs) in the temperature range $T_P/3 \lesssim T \lesssim T_P/2$ where T_P is the Peierls transition

temperature. It has been widely accepted that the freezing develops gradually and that the single-particle (Peierls) gap is the highest barrier that governs the activated dynamics of the complex relaxation. The recent extension of these measurements to lower frequencies and to lower T has shown that the real part of the dielectric constant ϵ' becomes strongly polydispersive. The magnitude of the peak in ϵ' increases and its position shifts to lower T when the frequency is decreased, pointing to a glassy transition temperature (13 K for TaS₃) [5]. On the other hand at even lower temperatures (below 1 K) the contribution to the specific heat of low-energy excitations (LEES) between CDW metastable states has been measured [6]. Moreover in the same temperature range energy relaxation with very low activation energies (1–2 K) has been observed and ergodicity breaking with evolving ‘aging’ effects has been recently demonstrated [6].

In this letter we present results of relaxation measurements in the spin-density wave (SDW) state of TMTSF₂PF₆ (TMTSF is tetramethyltetraselenafulvalene). We have performed two types of experiment: dielectric relaxation between 1 and 5 K and energy relaxation below 1 K. These measurements show two distinct dynamical regimes, which merge together around 2 K, a temperature we tentatively define as the onset of the glass transition (T_g). We reconcile these relaxational processes into the consistent picture of a glass transition. We will identify the dielectric relaxation, showing a characteristic freezing out at T_g , as the primary process, and the enthalpy relaxation, with low-energy excitation below T_g , as the secondary one.

The real and imaginary parts of AC conductivity of TMTSF₂PF₆ have been measured by the same improved technique as previously described [5]. The experimental window was in the frequency range from 100 Hz to 1 MHz and in the temperature range between 1 and 5 K. Measurements on three different samples with characteristic sizes (length, 3–5 mm; cross-sectional area, $100 \times 100 \mu\text{m}^2$) yielded the same qualitative behaviour. Due to a special method of contact preparation and a very low cooling rate ($\sim 0.5 \text{ K min}^{-1}$) in zero electric field we did not observe any appreciable resistance jumps upon cooling from 300 K to 1 K. A high value of the resistance ratio $R_{4.2}/R_{\text{min}} \sim 20$ indicates the good quality of the samples used. An additional electronic circuit has been built for keeping the voltage on the samples below the threshold value ($V_T \simeq 10 \text{ mV cm}^{-1}$ at 4 K) so that the system remained in the linear regime (pinned SDW).

The temperature dependence of ϵ' at various frequencies, from 111 Hz up to 100 kHz, is shown in the inset of figure 1. Between 3.5 K and 2.5 K, ϵ' shows a pronounced maximum, whose magnitude and position are frequency dependent. For lower frequencies the magnitude of the ϵ' maximum grows and its position is shifted towards lower T . Although the value of ϵ' is huge, it is not unexpected for the SDW condensate [7] and it is in qualitative agreement with earlier works [7, 8]. In the inset of figure 1, in addition to our data we have also drawn the results from [7] obtained at 10 kHz, which show the same temperature dependence up to the maximum at 2.5 K but there are no more data at higher T . In the temperature range below the ‘cusps’ ϵ' exhibits the typical dependence $\epsilon' \sim \omega^{-\alpha}$ with $\alpha \simeq 0.6\text{--}0.8$, as in the case of variable-range hopping conductivity, which is the manifestation of a broad distribution of SDW metastable states.

Similar cusp-like behaviour with slowing down upon decreasing temperature is a very well known characteristic of various glass-forming materials such as spin glasses [9], orientational glasses [10] and CDW glasses [5] when their freezing temperature is approached. When the frequency of the experimental probe becomes larger than the inverse τ^{-1} of the characteristic relaxation time, dynamical retarding effects occur. The frequency sensitivity of the temperature T_m of the maxima of ϵ' or χ' has been widely used as the criterion to classify different glasses: while an Arrhenius law is predicted for non-interacting clusters

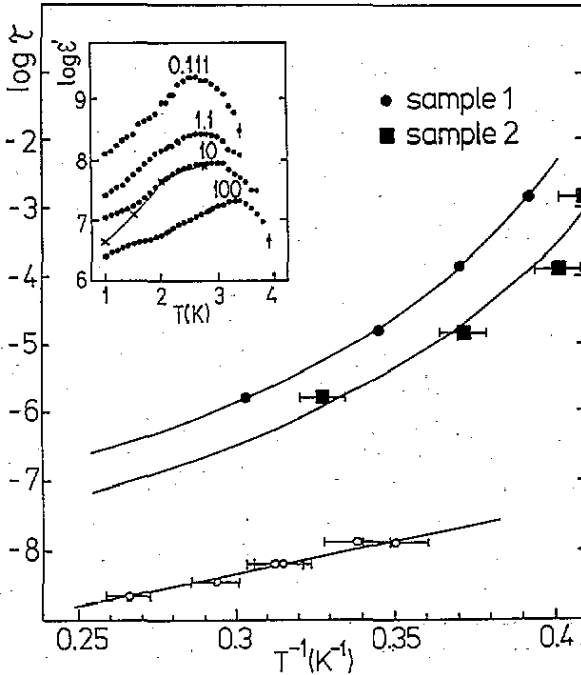


Figure 1. The variation of relaxation time τ (the logarithm of time in s) in dielectric relaxation for two samples of $\text{TmRSE}_2\text{PF}_6$ as a function of T^{-1} . The full lines are the best fits to the Volger-Fulcher law or the critical slowing-down law (with parameters given in the text). The dashed line represents the activated behaviour obtained by NMR experiment in the MHz range (taken from [12]). The inset shows the cusp-like behaviour of the real part of the dielectric constant ϵ' for frequencies (given in kHz) from which the dielectric relaxation time has been obtained. For comparison we show (full line) the results at 10 kHz reported in [7].

with $T_c = 0$, the curvature in the $\log \tau = f(1/T_m)$ plot shown for two samples in figure 1 indicates that either the phenomenological Vogel-Fulcher (VF) law with

$$\tau/\tau_0 = \exp[E_0/k(T - T_0)]$$

or the critical slowing down (CSD) behaviour with

$$\tau/\tau_0 = (1 - T/T_c)^{-z\nu}$$

should be valid. The VF law implies a characteristic local ordering temperature T_0 arising from interactions between clusters with the longest relaxation time. The relaxation is controlled by energy barriers of the order of E_0 . CSD behaviour is associated with a real transition at T_c where τ diverges. From the VF law one obtains $10^{-9} < \tau_0 \leq 10^{-8}$ s, $8 < E_0 < 10$ K, $1.8 < T_0 < 2$ K, and from CSD one obtains $10^{-10} < \tau_0 \leq 10^{-9}$ s, $6 < z\nu < 8$ and $2.2 < T_c < 2.3$ K for sample 1. The quality is equally good for both fits (with slightly different fitting parameters for the two samples) and they cannot be distinguished in this experimental window. This is a typical behaviour for the primary, α , process with a freezing out of dynamics at T_c .

Studies of the NMR lattice relaxation rate, T_1^{-1} , in the SDW state have shown that the main behaviour of T_1^{-1} originates from phason fluctuations. A rapid drop of T_1^{-1} below

3.5 K has been reported. It was initially suggested that this drop reflected a phase transition in the SDW state [11]. This feature has also been explained [12] as a dynamic effect resulting from the progressive slowing down of phason fluctuations when T is lowered with an activation energy $\Delta/k_B = 18.3 \pm 4$ K, which is close to the single-particle gap ($\Delta = 21$ K). We have also plotted in figure 1 the data of the NMR frequency of the peak in T_1^{-1} for protons as measured in [12]. These two sets of data are not contradictory, but this apparent discrepancy between the low-frequency dielectric relaxation window and the NMR window (MHz range) clearly suggests the importance of time-scale effects in SDW glasses. A similar effect recently observed in the dielectric relaxation of one deuteron glass has been explained as a different manifestation of the frequency filter on the wide distribution function [13]. An Arrhenius behaviour is characteristic of the relaxation frequencies near the high-frequency edge, whereas there is a divergence of the relaxation time for the lower-frequency edge. This empirical model may be regarded as perfectly general. Although it does not provide insight into the microscopic mechanism of glassy relaxation, it gives clear evidence that the maximum time scale diverges on approaching the freezing transition [13].

We have already shown for some CDW systems [6] that the relaxation dynamics as exhibited in the enthalpy relaxation at very low temperature ($T < 1$ K) is very similar to that occurring in disordered systems such as glassy polymers and spin glasses below their freezing temperature. Low- T thermodynamic measurements are presumably the best method for revealing the LEEs between metastable states. We have measured the extra contribution of the SDW LEE modes to the specific heat at low T in addition to the phonon contribution [14]. As in the case of our previous studies on CDW materials [6], we observed a progressive deviation from exponential decay below 0.6 K, announcing new, very slow relaxations, which originate from these LEE modes, typical of glassy states.

In this temperature range, we studied the energy relaxation on a sample of about 150 mg with the same sample arrangement [14] as in the case of CDW materials [6]. Looking for time-scale effects we scanned the enthalpy relaxation after varying the duration of the thermal perturbation (t_d , 1 s up to 14 h) but always keeping about the same magnitude ($\Delta T_0/T$ of the order of a few per cent). When the perturbation is switched off the relaxation $\Delta T/\Delta T_0$ as shown in figure 2(a) deviates from an exponential decay (which for $t_d = 1$ s is represented by the full line) and shows a strong dependence on t_d , so that it occurs at longer time for large t_d . In all cases the relaxation can be approximately fitted by a stretched exponential. The energy relaxation rate is defined as $d[\Delta T(t)/\Delta T_0]/d \log t$. We show in figure 2(b) that it exhibits a peak at t^m . When the duration of the perturbation (or waiting time t_w in [6]) is increased, t^m is shifted towards longer times. We obtain more pronounced 'aging' effects in $\text{TMTSF}_2\text{PF}_6$ than in CDW systems, especially TaS_3 , for which these effects were the strongest (there are more details in [6] and [15]). However, these aging effects saturate beyond an ergodic time t_e , revealing a cross-over [6] between a non-equilibrium ground state and a thermodynamical equilibrium state (shown in the inset of figure 2).

We have determined the ergodic time t_e at each temperature. The variation of t_e as a function of $1/T$ plotted in figure 3 shows that the relaxation of the remaining LEE modes in $\text{TMTSF}_2\text{PF}_6$ is thermally activated with an activation energy of $E_a \simeq 1.8$ K (see the inset of figure 3).

The separation or bifurcation [16] between the two different relaxation processes at low T in $\text{TMTSF}_2\text{PF}_6$ is clearly visible in figure 3. If one extrapolated the temperature dependence of both relaxation processes, the cross-over between them would occur around 2 K, a temperature we define as the glass transition temperature T_g [2, 10, 16]. This approach is strongly supported by recent direct evidence for a calorimetric glass transition [17]. Indeed, the strong hysteretic effects and the very specific role of isothermal annealing around the

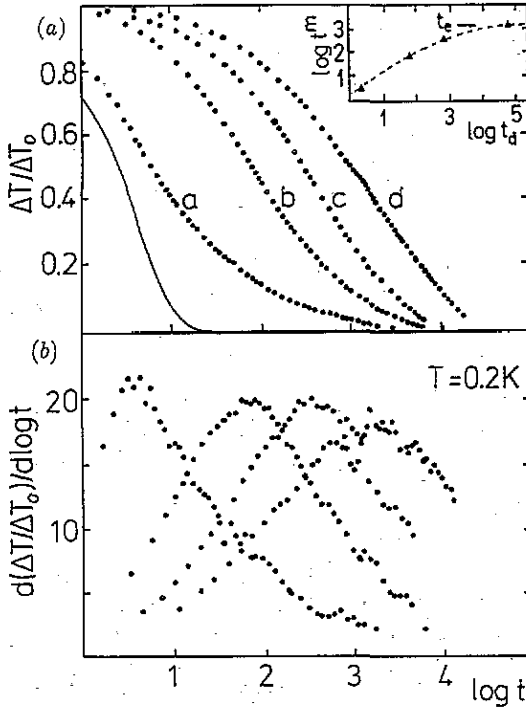


Figure 2. (a) Non-exponential enthalpy relaxation of $\text{TMTSF}_2\text{PF}_6$ at $T = 0.2$ K after switching off the thermal perturbation for various durations of the heat input: a, 1–2 s; b, 1 min; c, 10 min; d, 11 h. The logarithmic scales correspond to time in seconds. The corresponding exponential relaxation after a 1 s pulse is shown by the full line. (b) Enthalpy relaxation rates of $\text{TMTSF}_2\text{PF}_6$ in the same conditions as in (a). The inset shows the saturation of the aging effect when the system reaches equilibrium and the determination of the relaxation time t_e at this temperature.

specific heat anomaly at ~ 3 K present the very well known characteristics of the typical glass transition in supercooled liquids. In figure 3 we have also plotted the data for the SDW pinned mode obtained by microwave measurements [18].

We shall now briefly discuss these results in the general frame of the glass transition. As stated in section 1, it is widely accepted that a secondary β relaxation with an Arrhenius activation energy is a basic feature of the glass transition [1, 2]. In contrast to the α process which freezes out at T_g , the β process also persists below T_g . In this context we propose the following scenario for SDWs. It is also appropriate to CDWs because there are no essential differences between these two types of DW except that there is no lattice distortion in SDWs. In the modulated phase below the transition temperature, relaxation processes that we can identify as α processes are essentially elastic [3, 19]. The screening of the DW deformations is progressively frozen when T is reduced because of the exponential reduction of normal carriers. The dominant mechanism of energy dissipation is given by the damping parameter, or the 'viscosity' $\eta \sim \rho_n$, the normal resistivity, and consequently the main relaxation time is thermally activated with an activation energy of the order of the DW gap. It is believed that this screening effect is the unique feature that dominates the dielectric response down to the lowest temperatures [3, 19]. However, the monotonic increase of ϵ' as observed in figure 1 for $\text{TMTSF}_2\text{PF}_6$ (as for TaS_3 in [5]) suggests a divergence of the polarizability when T is reduced. If above T_g the relaxation time is given by an Arrhenius function, near T_g τ varies faster than this as shown in figure 1.

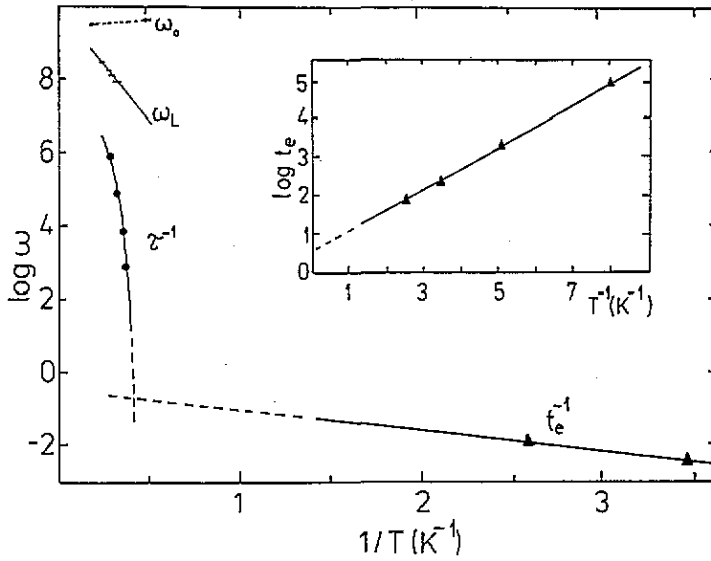


Figure 3. The variation of the inverse τ^{-1} and t_e^{-1} of the relaxation time in dielectric (\bullet) and energy relaxation (\blacktriangle) respectively, with T^{-1} . This shows the crossing of the two relaxation processes in the region of the glass transition, which indicates the typical behaviour of primary α relaxation and secondary β relaxation. The variation of the Larmor frequency ω_L (in rad s^{-1}) in NMR experiments from [12] and the variation of the sdw pinned mode ω_0 from [18] are also plotted. In the inset the activated behaviour of the enthalpy relaxation t_e in the whole temperature range investigated is shown.

Following the description in the phase-space landscape it may be said that in the vicinity of T_g the DW 'cage' (domains of correlated DW phase) is frozen, or trapped in a deep minimum. However, this potential well can be corrugated and exhibit local small minima. So, rearrangements involving lower barriers can still exist and give rise to secondary β relaxation. These minima correspond to degrees of freedom not affected by the glass transition. As in supercooled glasses [2], we associate these excitations with topological defects, which in the DW superstructure are presumably dislocation loops and/or disclinations. Certainly a dislocation loop cannot jump as a whole rigid entity; there must be a sequential or cooperative character to the process involving only localized portions of any loop. The relaxation process that we have observed may correspond to such a hopping motion of local parts of domain walls or dislocation loops. The observed log-normal form in the distribution of enthalpy relaxation indicates that the underlying distribution of the energy barriers is Gaussian. In addition, the relaxation time for this relaxation exhibits an Arrhenius behaviour; altogether they show the very well established characteristics of slow β relaxation.

The problem of length scales is closely related to the understanding of the glass transition. The characteristic length ξ_c of the dynamic glass transition is required in the cooperativity concept [20,21]. The breaking down of cooperativity above T_c or T_0 is strongly manifested in the dynamics as ξ_c somehow defines the size of the scatterers in the system. In ordinary molecular glass-forming liquids this happens in the GHz range, which is in agreement with the characteristic length of a few nanometres [22]. Dielectric measurements in PF_6 show new features in the real part of ϵ' only at frequencies below the MHz range, which implies a ξ_c of at least few hundred nanometres.

We consider that the assertion of a glassy transition is the key for explaining many phenomena in $\text{TMTSF}_2\text{PF}_6$ in this temperature range that are not understood: the sudden drop below 2.6 K of the electrical conductivity carried by the sliding SDW [23]; the freezing out of the internal SDW deformations [7] below 2 K; the spin lattice relaxation T_1^{-1} anomaly [11, 12]. From the calorimetric glass transition study [17], it has been pointed out that the estimated configurational entropy above the glass transition overcomes the electron entropy, so there should be underlying electron-phonon interaction, which is often neglected in SDWs. Presumably this coupling to the lattice should occur through the phase deformation of the DW. Moreover, the non-linear properties should be also affected by freezing processes on approaching the glass transition, and the I - V curves recently published in this temperature range for both systems, CDWs [24, 25] and SDWs [7], have to be examined in this respect.

In conclusion we have distinguished two relaxation processes at low temperatures in $\text{TMTSF}_2\text{PF}_6$, which merge together around 2 K, a temperature we define as the freezing temperature T_g . Above T_g the relaxation rate determined by dielectric relaxation follows a VF law or a critical slowing-down behaviour. Below T_g energy relaxation follows an activated process with an activation energy of ~ 1.8 K, attributed to motion of the localized portions of SDW dislocations. The nature of the glass transition in the DW state is a very unique one as it concerns collective modes in a system essentially characterized by the electronic Fermi surface. The real nature of the remaining LEE has to be found even if it looks natural to consider DW topological defects [5, 6].

References

- [1] For recent reviews see Campbell I A and Giovannello C (ed) 1990 *Relaxation in Complex Systems and Related Topics* (New York: Plenum)
1991 *J. Non-Cryst. Solids* **131-133**
- [2] Goldstein M 1969 *J. Chem. Phys.* **51** 3728
Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 2372
- [3] Littlewood P B and Rammal R 1988 *Phys. Rev. B* **38** 2675 and references therein
- [4] Fleming R M and Cava R J 1989 *Low-Dimensional Electric Properties of Molybdenum Bronzes and Oxides* ed C Schlenker (Dordrecht: Kluwer) p 259
- [5] Nad' F Ya and Monceau P 1993 *Solid State Commun.* **87** 13; 1993 *J. Physique Coll.* IV **3** C2 343
- [6] Biljaković K, Lasjaunias J C, Monceau P and Lévy F 1991 *Phys. Rev. Lett.* **67** 1902
Biljaković K, Lasjaunias J C and Monceau P 1991 *J. Non-Cryst. Solids* **131-133** 1254
- [7] Mihaly G, Kim Y and Grüner G 1991 *Phys. Rev. Lett.* **67** 2713; 1991 *Phys. Rev. Lett.* **66** 2806
- [8] Kriza G, Kim Y, Beleznyay A and Mihaly G 1991 *Solid State Commun.* **79** 811
- [9] For a review see Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801
- [10] For a review see Höchli U T, Knorr K and Loidl A 1990 *Adv. Phys.* **39** 405
- [11] Takahashi T *et al* 1987 *Synth. Met.* **19** 225
Takahashi T, Harada T, Kobayashi Y, Kanoda K, Suzuki K, Murata K and Saito G 1991 *Synth. Met.* **41** 3985
- [12] Wong W H, Hanson M E, Alavi B, Clark W G and Hines W A 1993 *Phys. Rev. Lett.* **70** 1882
Clark W G, Hanson M E, Wong W H and Alavi B 1993 *J. Physique Coll.* IV **3** C2 235
- [13] Kutnjak Z, Filipić C, Levstik A and Pirc R 1993 *Phys. Rev. Lett.* **70** 4015
- [14] Lasjaunias J C, Biljaković K, Monceau P and Bechgaard K 1992 *Solid State Commun.* **84** 297
- [15] Biljaković K, Lasjaunias J C and Monceau P 1993 *J. Physique Coll.* IV **3** C2 335
- [16] Rössler E 1991 *J. Non-Cryst. Solids* **131-133** 242 and private communication
- [17] Lasjaunias J C, Odin J, Biljaković K, Monceau P and Bechgaard K 1993 *J. Physique Coll.* IV **3** C2 365
Lasjaunias J C *et al* to be published
- [18] Donovan S, Kim Y, Degiorgi L and Grüner G 1993 *J. Physique* I **3** 1493
- [19] Littlewood P B 1987 *Phys. Rev. B* **36** 3108
- [20] Adam G and Gibbs J H 1965 *J. Chem. Phys.* **43** 139
- [21] Ngai K L 1991 *J. Non-Cryst. Solids* **131-133** 80

- [22] Donth E 1982 *J. Non-Cryst. Solids* **53** 325
- [23] Tomić S, Cooper J R, Kang W, Jérôme D and Maki K 1991 *J. Physique* **11** 1603
- [24] Itkis M E, Nad' F Ya and Monceau P 1990 *J. Phys.: Condens. Matter* **2** 8327
Nad' F Ya 1993 *Pis. Zh. Eksp. Teor. Fiz.* **58** 186
- [25] Zaitsev-Zotov S V 1993 *Phys. Rev. Lett.* **71** 605